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(71)Applicant : SHIPLEY CO LLC

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(72)Inventor : ADAMS TIMOTHY G  
PAVELCHEK EDWARD K  
SINTA ROGER F  
DOCANTO MANUEL  
ROBERT F BLACKSMITH  
TREFONAS PETER III

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## (54) ANTIREFLECTION COATING COMPOSITION

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a novel light absorbing crosslinked composition suitable for use as an antireflection composition and particularly suitable for forming an image with a short wavelength as 193 nm.

**SOLUTION:** A layer of an antireflection composition containing a resin binder having phenyl groups is disposed on a substrate and cured. A layer of a photoresist composition is disposed on the cured layer, exposed with activating radiation and developed to form a photoresist relief image. In this method, the ARCs are employed together with the overcoated resin layer using the ARCs as a base layer, contain a novel ARC resin binder in general, and effectively absorb reflected exposure radiation of <200 nm wavelength.

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(71) 出願人 596156688  
 シップレーカンパニー エル エル シー  
 Shipley Company, L.  
 L. C.  
 アメリカ合衆国01752マサチューセッツ州  
 マルボロ フォレスト・ストリート455

(72) 発明者 ティモシー・ジー・アダムス  
 アメリカ合衆国01752マサチューセッツ州  
 サドバリー ダットン・ロード 137

(74) 代理人 100102668  
 弁理士 佐伯 憲生

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(54) 【発明の名称】 反射防止コーティング組成物

(57) 【要約】 (修正有)

【課題】 反射防止組成物 (A R C) としての使用に好適な、特に193nmのような短波長での画像形成に好適な、新規な光吸収性架橋性組成物を提供する。

【解決手段】 (a) 基板の上に、フェニル基を有する樹脂バインダーを含む反射防止組成物の層を設けること； (b) 反射防止組成物層を硬化すること； (c) 反射防止組成物の層の上にフォトレジスト組成物の層を設けること； (d) フォトレジスト層を活性化照射光で露光し、そして露光したフォトレジストの層を現像すること；を含む、フォトレジストレリーフ画像を形成するための方法。

【効果】 A R C類は、好ましくは上塗りされたレジスト層 (すなわちA R C類を底層として) と共に使用され、一般に、新規なA R C樹脂バインダーを含み、反射された200nm未満の露光照射光を効果的に吸収することができる。

【特許請求の範囲】

【請求項1】 (a) 基板の上に、フェニル基を有する樹脂バインダーを含む反射防止組成物の層を設けること；

(b) 反射防止組成物層を硬化すること；

(c) 反射防止組成物の層の上にフォトレジスト組成物の層を設けること；

(d) フォトレジスト層を活性化照射光で露光し、そして露光したフォトレジストの層を現像すること；を含む、フォトレジストレリーフ画像を形成するための方法。

【請求項2】 フォトレジスト層を、約200nm未満の波長を有する活性化照射光で露光する、請求項1に記載の方法。

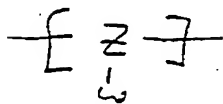
【請求項3】 フォトレジスト層を、約193nmの波長を有する活性化照射光で露光する、請求項1に記載の方法。

【請求項4】 反射防止組成物の樹脂の主鎖に、フェニル基が直接懸架している、請求項1に記載の方法。

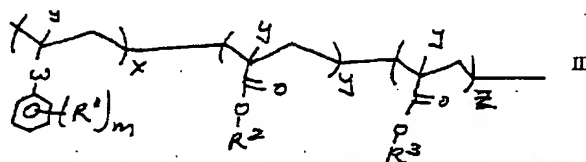
【請求項5】 フェニル基が反射防止組成物の樹脂の主鎖に懸架しており、そして樹脂の主鎖とフェニル基との間にいかなるアルキル単位も介在しない、請求項1に記載の方法。

【請求項6】 反射防止組成物の樹脂が次式I：

【化1】



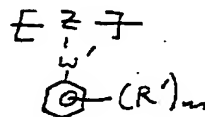
(式中、Wは、化学結合、アルキル結合、またはエステル結合；各R'は、水素、置換または非置換のアルキル、置換または非置換のアルコキシ、エステル、置換または非置換のアルカノイル、置換または非置換の炭素環式アリール、または置換または非置換のアラルキル；mは、0から5までの整数；および各Zは、ポリマー単位の間の独立した結合基である。)の単位を含む請求項1に記載の方法。



(式中、Wは、化学結合、アルキル結合、またはエステル結合；各R'は、水素、置換または非置換のアルキル、置換または非置換のアルコキシ、エステル、置換または非置換のアルカノイル、置換または非置換の炭素環式アリール、または置換または非置換のアラルキル；R2およびR3は、それぞれ異なる独立の置換または非置換のアルキルまたは置換または非置換の炭素環式アリール；各Yは、独立の水素または置換または非置換のC1-6アルキル；そしてx、yおよびzは、樹脂中のそれぞれの単位のモル%である。)の単位を含む請求項1に記載の方法。

【請求項7】 反射防止組成物の樹脂が次式IA：

【化2】

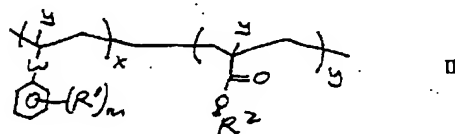


(式中、W'は、化学結合またはエステル結合；各R'は、水素、置換または非置換のアルキル、置換または非置換のアルコキシ、エステル、置換または非置換のアルカノイル、置換または非置換の炭素環式アリール、または置換または非置換のアラルキル；mは、0から5までの整数；および各Zは、ポリマー単位の間の独立した結合基である。)の単位を含む請求項1に記載の方法。

【請求項8】 反射防止組成物の中の樹脂がアクリレート樹脂である請求項1に記載の方法。

【請求項9】 反射防止組成物の樹脂が次式II：

【化3】



(式中、Wは、化学結合、アルキル結合またはエステル結合；各R1は、水素、置換または非置換のアルキル、置換または非置換のアルコキシ、エステル、置換または非置換のアルカノイル、置換または非置換の炭素環式アリール、または置換または非置換のアラルキル；R2は、置換または非置換のアルキルまたは置換または非置換の炭素環式アリール；各Yは、独立の水素または置換または非置換のC1-6アルキル；そしてxおよびyは樹脂中のそれぞれの単位のモル%；の単位を含む請求項1に記載の方法。

【請求項10】 上記一般式IIにおいて、R2が水酸基を含む請求項9に記載の方法。

【請求項11】 反射防止組成物の樹脂が次式III：

【化4】

換のアルキルまたは置換または非置換の炭素環式アリール；各Yは、独立の水素または置換または非置換のC1-6アルキル；そしてx、yおよびzは、樹脂中のそれぞれの単位のモル%である。)の単位を含む請求項1に記載の方法。

【請求項12】 上記一般式IIIにおいて、R2または

R<sub>3</sub>置換基の少なくとも1つが水酸基を有する請求項1に記載の方法。

【請求項13】反射防止組成物が熱酸発生剤化合物を含む請求項1に記載の方法。

【請求項14】フォトレジスト組成物層を設ける前に反射防止組成物を熱的に硬化する請求項1に記載の方法。

【請求項15】反射防止組成物が光酸発生剤を含み、その光酸発生剤がフォトレジスト組成物層を露光するまで実質的に活性化されない請求項1に記載の方法。

【請求項16】反射防止組成物が架橋剤物質を含む請求項1に記載の方法。

【請求項17】フォトレジスト組成物が化学的に増幅されたポジ型である請求項1に記載の方法。

【請求項18】(a)基板の上に、フェニル基を有する樹脂バインダーを含む反射防止組成物の層を設けること；

(b)反射防止組成物の層の上にフォトレジスト組成物の層を設けること；

(c)フォトレジスト層を活性化照射光で露光し、そして露光したフォトレジストの層を現像すること；を含む、フォトレジストレリーフ画像を形成するための方法。

【請求項19】フォトレジスト層を約200nm未満の波長を有する活性化照射光で露光する請求項18に記載の方法。

【請求項20】反射防止組成物の樹脂の主鎖にフェニル基が直接懸架している請求項18に記載の方法。

【請求項21】(1)フェニル基を有する樹脂を含む反射防止組成物の塗布層；

(2)反射防止組成物層の上にフォトレジスト層の塗布層；をその上に有する塗布された基板を含む塗布された基板。

【請求項22】上塗りされたフォトレジストを200nm未満の波長において画像形成するために使用される、フェニル基を有する樹脂を含む底層の反射防止組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、基板から上塗りされたフォトレジスト層への露光照射光の後戻りによる反射を減少する組成物に関する。より詳細には、本発明は、193nm照射光のような200nm未満の照射光を含む短波長露光照射光を、効果的に吸収する樹脂バインダーを含む反射防止被覆組成物類(ARCs)に関する。

【0002】

【従来の技術】フォトレジストは画像を基板に転写するために使用される感光膜である。フォトレジストの塗布層は基板の上に形成され、次いで、フォトレジスト層はフォトリソを通して活性化照射源に露光される。フォトリソは、活性化照射光に対して不透明な領域と、活

性化照射光に対して透明な他の領域とを有する。活性化照射光に露光されると、フォトレジスト被膜が光に誘起された化学的変性(photo induced chemical transformation)を生じ、それによってフォトリソのパターンがフォトレジストを塗布した基板に転写される。露光の後、フォトレジストを現像すると、基板の選択的加工が可能なレリーフ画像が得られる。

【0003】フォトレジストはポジ型でもネガ型でも可能である。大抵のネガ型フォトレジストの場合、塗布層の活性化照射光に露光される部分は、フォトレジスト組成物の感光性化合物と重合可能な試薬との間の反応において、重合または架橋を行う。従って、露光された塗布部分は露光されない部分よりも現像溶液により溶解しにくくなる。ポジ型フォトレジストの場合は、露光された部分は現像溶液により溶解しやすくなり、一方露光されない領域は、比較的現像液により溶解しにくい状態を維持する。フォトレジスト組成物は当業者には公知であり、デフォレスト(Deforest)による「フォトレジスト材料および方法」(Photoresist Materials and Processes)(McGraw Hill Book Company, New York, 1975)の第2章、およびモリー(Moreay)の「半導体リソグラフィ、原理、実際および材料」(Semiconductor Lithography, Principles Practices and Materials)(Plenum Press, New York)の第2章および第4章に記載されていて、この両文献については、フォトレジスト組成物およびその製造法と使用方法に関する教えについて、本発明においても参照している。

【0004】フォトレジストの主な用途は半導体においてであり、1つの目的は、シリコンまたはヒ化ガリウムなどのような高度に研磨された半導体の薄片を、回路としての機能を発現させるために、好ましくはミクロンまたはサブミクロンの幾何学的な模様、電子の伝導通路の複雑なマトリックスに変換することである。適切にフォトレジストを加工することがこの目的を達成するための鍵である。種々のフォトレジスト加工工程の間には強い相互依存性があるが、高解像度のフォトレジスト画像を得るにあたっては露光がより重要な工程の1つであると考えられている。

【0005】しばしば、フォトレジストを露光するために使用する活性化照射光の反射が、フォトレジスト層においてパターン形成された画像の限度を呈することがある。照射光が基板/フォトレジスト界面から反射すると、露光の間フォトレジストの中の照射強度が変化することがあり、それによって現像時にフォトレジストの線幅が不均一になる。照射光が基板/フォトレジスト界面から露光の目的としないフォトレジスト領域へ散乱する

こともあり、この場合も線幅がばらつくことになる。散乱や反射の程度は領域によって典型的に変化し、これによってもさらに線幅が不均一になる。基板の形状における変化も解像度に限度を呈する反射問題を引き起こす。

【0006】半導体デバイスが高密度となっている最近の傾向から、産業界では露光源の波長を、遠紫外（DUV）光（300nm以下の波長）、KrFエキシマーレーザー光（248.4nm）、ArFエキシマーレーザー光（193nm）、電子ビームおよび軟X線へと短くする傾向がある。フォトリソ被膜に画像形成するために短くした波長を使用することから、結果として、一般に下層の基板の表面と同様に上層のレジスト表面からの反射が増加した。従って、より短い波長を使用することが基板表面からの反射の問題を大きくしてきた。

【0007】反射光の問題を少なくするため使用される別の手法では、基板表面とフォトリソ被覆層との間に挿入する照射光吸収層を使用してきた。例えば、PCT出願公開公報第90/03598号（W090/03598）、ヨーロッパ特許出願公開公報第0639941号（EP, A1, 0, 639, 941）および米国特許第4,910,122号、同第4,370,405号および同第4,362,809号を参照されたい。これらは全て、反射防止（ハレーション防止）組成物およびその使用法の開示に関して本発明で参照している。このような層は、前記文献中でも反射防止層またはARC（反射防止組成物）という表現で述べられている。シップレー社（Shipley Co.）のヨーロッパ特許出願公開公報第542008号（EP, A1, 542, 008）には、極めて有用なハレーション防止（反射防止）組成物が開示されている。

【0008】

【発明が解決しようとする課題】先行技術におけるARC組成物が多くの反射防止用途に有効であることが見出されている一方で、先行技術の組成物には、特に短波長画像形成用途に使用した場合いくつかの性能上の制約がある。従って、新規な反射防止コーティング組成物を持つことが望まれる。特に、193nmのような200nm未満（sub-200nm）の照射光を含む、短波長の照射光の望ましくない反射を効果的に吸収する新規な反射防止コーティング組成物が望まれる。

【0009】

【課題を解決するための手段】本発明は、特に193nm画像形成のような短波長画像形成用途に対し、反射防止コーティング組成物（ARC）として使用するのに好適な新規な光吸収組成物を提供する。本発明のARC類は、一般的に、短波長露光照射光を効果的に吸収してこの照射光の反射を減少させる樹脂バインダーを含み、必要により架橋剤成分も含む。

【0010】本発明のARC類の好ましい樹脂バインダーは、ポリマー主鎖に好ましくは懸架したフェニル単位

を含む。本発明の特に好ましいARC樹脂バインダーは、ポリマー主鎖と懸架したフェニル単位との間に介在する如何なるアルキル（例えば、置換または非置換の $(-CH_2-)_n$ で、nは1から約6または8である。）単位も有しない。例えば、好ましい懸架した基は、置換または非置換のスチレン、置換または非置換のイソプロピルスチレン、置換または非置換のアクリル酸フェニル、及び、置換または非置換のメタクリル酸フェニルの重合により得られるものを含む。本発明で述べる、ポリマー主鎖から「直接懸架した（directly pendant）」フェニル基とは、置換または非置換のスチレンまたは置換または非置換のイソプロピルスチレン単位の重合によって得られるように、ポリマー主鎖とフェニル基との間にアルキル基または他の基が介在しないことを示す。

【0011】しかしながら、あまり好ましくはないが、本発明は、例えばメタクリル酸-2-フェニルエチルおよびその類似化合物の重合により得られるような、ポリマー主鎖とフェニル基の間にアルキル（例えば、置換または非置換の $(-CH_2-)_n$ で、nは1から約6または8である。）結合が介在する懸架したフェニル基を持つ樹脂バインダーを有するARC類も包含する。

【0012】フェニル発色団部分を持った反射防止組成物樹脂バインダーは、好適にはコポリマーであり、好ましくは2またはそれ以上の異なるモノマーの重合によるものであって、そのモノマーの少なくとも1つはフェニル発色団グループを含むものである。例えば、好ましい別のARC樹脂単位は、例えば、メタクリル酸-2-ヒドロキシエチル、アクリル酸-2-ヒドロキシエチルおよびそれらの類似化合物のようなヒドロシアクリレート；メタクリル酸メチル、アクリル酸メチル、メタクリル酸ブチル、アクリル酸ブチルおよびそれらの類似化合物のような $C_{1-12}$ アクリレートのようなアクリレートモノマーの重合によって得られるものを含む。フェニル発色団単位を含むアクリレート樹脂は、一般に本発明のARC類の中で使用されることが好ましい。本発明のARC類を架橋するために、好ましくはARC樹脂は硬化反応を推進するための水酸基または他の反応性部分を有する。

【0013】本発明は、さらにレリーフ画像を形成する新規な方法、および本発明のARC組成物単独またはフォトリソ組成物との組み合わせで塗布された基板を含む新規な製造技術を提供する。本発明の他の態様は以下に開示される。

【0014】

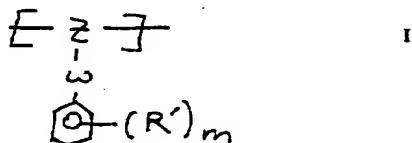
【発明の実施の形態】本発明の反射防止組成物の樹脂バインダー組成物は、短波長の画像形成システムと共に使用するのが好ましく、200nm未満の反射、特に193nmの反射を効果的に吸収する。

【0015】特に、好ましい本発明のARC樹脂バイン

ダーは、懸架したフェニル基を持つ。例えば、好ましい樹脂は次式 I で示されるフェニル単位を持つ。

【0016】

【化5】



【0017】(式中、Wは、化学結合、アルキル結合、例えば置換または非置換の $(-CH_2-)_n$ で、nが1から約6または8、またはエステル結合(すなわち、

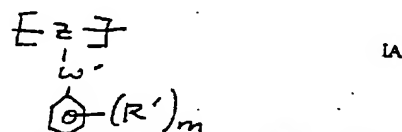
$(C=O)O$ ) ; 各 $R'$  は、水素またはハロゲン(F、Cl、Br、またはI)のような非水素置換基 ; 好ましくは1個から約8個の炭素原子を持つ置換または非置換のアルキル ; 好ましくは1個から約8個の炭素原子を持つ置換または非置換のアルコキシ、 $-C(=O)OZ$ のような置換または非置換のエステルで、Zは $C_{1-8}$ の置換または非置換のアルキル ; 例えばアシルおよび類似基である $C_{1-8}$ アルカノイルのような置換または非置換のアルカノイル ; 置換または非置換の炭素環式アリール、特にフェニル ; 置換または非置換のアラルキル、特にベンジル $(-CH_2C_6H_5)$  ; および類似基 ; mは、0(懸架したフェニル基が完全に水素で置換されている場合)から5の整数 ; そしてZは、ポリマーのモノマー単位間の結合基であり、例えば炭素-炭素二重結合

のようなモノマー単位の反応成分で、重合して、例えば、置換または非置換のアルキレン、好ましくは $C_{1-4}$ アルキルで置換されたまたはされていない $C_{1-3}$ アルキレンを与える。)

【0018】前述のように、より好ましい樹脂は、懸架したフェニル基を持つが、ポリマー主鎖と懸架したフェニル基の間に介在するいかなるアルキル(例えば、置換または非置換の $(-CH_2-)_n$ で、nは1から約6または8である。)基も持たない樹脂、例えば次式IAで示されるフェニル単位を持つ樹脂である。

【0019】

【化6】

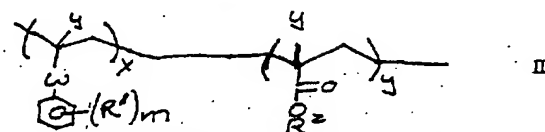


【0020】(式中、W'は、化学結合またはエステル結合(すなわち、 $(C=O)O$ ) ; 各 $R'$ 、mおよびZは、上記式Iで定義されたものと同じである。)

また前述のように、本発明の特に好ましいARC樹脂は、フェニル発色団単位を持つ繰り返し単位に加えてアクリレート単位を持つ。例えば、好ましい樹脂としては、次式IIで表わされる単位から成るアクリレートコポリマーが挙げられる。

【0021】

【化7】



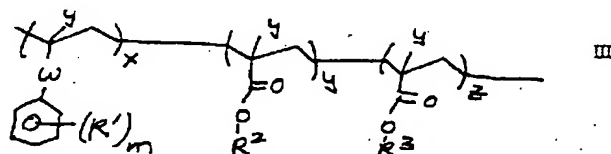
【0022】(式中、W、各 $R'$  およびmは、上記式Iで定義されたものと同じであり ;  $R_2$ は、好ましくは1から約20の炭素原子、より好ましくは1から約8ないし20の炭素原子の置換または非置換のアルキル基 ; フェニルなどのような置換または非置換の炭素環式アリール、または、置換または非置換のベンジル、2-フェニルエチルおよび類似基のような置換または非置換のアラルキルであり、そして好ましくは $R_2$ は非芳香族基である。各Yは、独立した、水素または置換または非置換の $C_{1-6}$ アルキル、そして好ましくは、各Yは、独立した、水素またはメチル ; 及び、xとyは、ポリマー中の

それぞれの単位のモルパーセントであり、好ましくはxは約5パーセントから約80ないし90パーセント、より好ましくは約10ないし15パーセントから約60ないし70パーセント、さらにより好ましくは約20パーセントから約50パーセントで、ポリマーの残りは $R_2$ 基または他の単位を含む単位を含む。)

【0023】3元コポリマーおよび他のより多元なコポリマー、例えば、次式IIIで示される単位を含むアクリレートコポリマーなどが特に好ましい。

【0024】

【化8】



【0025】(式中、W、各 $R'$  およびmは、上記式I

で定義されたものと同じであり ; 式中、 $R_2$ と $R_3$ は、

それぞれ異なり、式 I I 中の  $R_2$  で定義されたものと同じ基から独立に選ばれ；各 Y は、独立した、水素または置換または非置換の  $C_{1-6}$  アルキル、好ましくは、各 Y は、独立した、水素またはメチル；そして x、y および z は、ポリマー中のそれぞれの単位のモルパーセントであり、好ましくは、x は約 5 パーセントから約 80 ないし 90 パーセント、より好ましくは約 10 ないし 15 パーセントから約 60 ないし 70 パーセント、さらにより好ましくは x は約 20 パーセントから約 50 パーセントで、ポリマーの残りは  $R_2$  基と  $R_3$  基、または他の単位を含む単位から成る。）

【0026】上記式の好ましい  $R_2$  と  $R_3$  は、ヒドロキシ置換アルキル基、特に 2-ヒドロキシエチルおよびヒドロキシプロピルのような  $C_{1-6}$  ヒドロキシアルキル；メタクリル酸メチル、アクリル酸メチル、メタクリル酸エチル、アクリル酸エチル、メタクリル酸ヘキシル、アクリル酸ヘキシルの重合により得られるような脂環式  $C_{1-8}$  アルキル；および、好適にはシクロヘキシル、アダマンチル、イソボルニルおよび類似基等のような 3 個から約 20 個の炭素を持ち、対応するアクリレートおよびメタクリレートの重合により得られる環状アルキル基を含む。

【0027】前記したように、ARC 樹脂は懸架したシアノおよび無水イタコン酸基等の他の単位を持ってもよい。好ましくは、無水イタコン酸部分はポリマー主鎖に直接懸架する、すなわち当該部分は、ポリマー結合基と無水イタコン酸基の間に介在するアルキレン、アリールまたは他の基を持たずに、ポリマー結合基に直接懸架する。一方、該シアノ基は好ましくは（アクリロニトリルまたは類似物の重合により）該ポリマー主鎖に直接懸架するが、結合基が該シアノ基とポリマー結合基の間に介在してもよい。

【0028】本発明で論じられたように、ARC 樹脂または他の ARC あるいはレジスト成分の種々の部位は所望ならば置換されてもよい。「置換された」置換基は 1 個またはそれ以上の置換可能な位置、一般的には 1、2 または 3 位において、例えばハロゲン（特に、F、Cl または Br）；シアノ； $C_{1-8}$  アルキル； $C_{1-8}$  アルコキシ； $C_{2-8}$  アルケニル； $C_{2-8}$  アルキニル；ヒドロキシル；例えばアシルおよび類似基等のような  $C_{1-6}$  アルカノイル等のアルカノイル；等の 1 個またはそれ以上の好適な基で置換され得る。

【0029】本発明の ARC 類に使用される特に好ましいポリマーは、フェニル単位のモルパーセント（すなわち、式 I I I 中の x の値）が 10 パーセントから約 60 パーセント、より好ましくは約 10 ないし 15 パーセントから約 40 ないし 50 パーセント； $R_2$  は、置換または非置換のアルキル、特に 2-ヒドロキシエチル等の  $C_{1-6}$  ヒドロキシアルキルであり、 $R_3$  基を持つエステル単位のモルパーセント（すなわち、式 I I I 中の y の

値）が約 1 モルパーセントから 50 ないし 60 モルパーセント、より好ましくは約 10 モルパーセントから 40 ないし 50 モルパーセント； $R_3$  が、例えばメチル、エチル等または環状アルキル基などの  $C_{1-8}$  脂環式アルキル等の非置換アルキルであり、 $R_3$  基を持つエステル単位のモルパーセント（すなわち、式 I I I 中の z の値）が約 10 モルパーセントから 60 ないし 70 モルパーセント、より好ましくは約 20 ないし 30 モルパーセントから 40 ないし 50 モルパーセント；各 Y が、独立した、水素またはメチルである、上記式 I I I の 3 元コポリマーを含む。特に好ましい ARC 樹脂については後述の実施例を参照されたい。

【0030】本発明の ARC 樹脂バインダーは、同一モノマーまたは好ましくはコポリマーを得るための異なるモノマーを重合することにより好適に合成される。少なくとも 1 種の重合されたモノマーはフェニル基を含有する。反応温度は、使用する特定の試薬の反応性、及び反応溶媒（溶媒を使用する場合）の沸点によって変わり得るが、例えば、ラジカル開始剤の存在下で、好ましくは不活性雰囲気（例えば、窒素またはアルゴン）下、約 70℃ 以上のような高温で、種々の単位を提供するモノマーを反応させることによるフリーラジカル重合が好適に用いられる。反応条件例は後述の実施例を参照されたい。本発明の開示により、当業者は経験的にあらゆる特定の系に対しても好適な反応温度を決めることができる。所望ならば反応溶媒を使用してもよい。好適な溶媒としては、テトラヒドロフラン、プロパノールおよびブタノールのようなアルコール、並びにベンゼン、クロロベンゼン、トルエンおよびキシレンのような芳香族溶媒等が挙げられる。ジメチルスルホキシドとジメチルホルムアミドも好適である。また、重合反応は無溶媒でも進めることができる。種々のフリーラジカル開始剤を使って本発明のコポリマーを調製してもよい。例えば、V a z o 52（デュボン社）、アゾビス-2，2'-イソプロチロニトリル（AIBN）および 1，1'-アゾビス（シクロヘキサンカルボニトリル）のようなアゾ化合物を使用してもよい。過酸化物、過酸エステル、過酸および過硫酸塩も使用してよい。

【0031】ARC 樹脂バインダーは約 1，000 から約 10，000，000 ダルトン、より一般的には約 5，000 から約 1，000，000 ダルトンの重量平均分子量（ $M_w$ ）、および約 500 から約 1，000，000 ダルトンの数平均分子量（ $M_n$ ）を持つことが好ましい。本発明のポリマーの分子量（ $M_w$  及び  $M_n$ ）はゲル浸透クロマトグラフィによって好適に求められる。

【0032】本発明の樹脂バインダーは、例えば 200 nm 未満、特に 193 nm の短波長で良好な吸光度を示すものが好ましい。より詳細には、本発明の好ましい樹脂バインダーは、約 193 nm においてミクロン当たり少なくとも約 3 吸光度（吸光度/ $\mu$ ）の光学密度、好ま

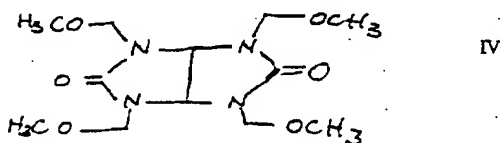
しは193nmにおいて約5から20またはそれ以上のミクロン当たりの吸光度、より好ましくは193nmにおいて約8から16またはそれ以上のミクロン当たりの吸光度を持つ。特徴的な樹脂に必要なより高い吸光度の値は、樹脂の発色団単位のパーセントを増やすことによって得ることができる。また、本発明の反射防止組成物は、フェニル発色団単位を持つ樹脂と共存する共樹脂 (co-resin) として、フェニル発色団単位を持たない樹脂を含有することができる。

【0033】本発明の反射防止組成物の樹脂バインダー成分の濃度は、比較的広い範囲で変化させることができ、樹脂バインダーは、通常、ARCの全乾燥成分の約50から95重量パーセント、さらに一般的には全乾燥成分 (溶媒キャリアを除いた全成分) の約60から90重量パーセントまでの濃度で使用する。

【0034】本発明の架橋型ARCは、架橋剤成分または物質も含む。種々の架橋剤を使用することができ、その中には前記のシプレー社 (Shipley Co.) のヨーロッパ特許出願第542008号に開示されているARC架橋剤類も挙げられる。架橋剤としては、メトキシメチル化グリコウリル (glycouril) のような低塩基度の架橋剤が特に好ましい。特に好ましい架橋剤としては、下記の構造式IVに対応するメトキシメチル化グリコウリルがある。

【0035】

【化9】



【0036】該メトキシメチル化グリコウリルは公知の手順で調製できる。また、この化合物は、アメリカンシアナミド社 (American Cyanamid Co.) からパウダーリンク (Powderlink) 1174の商品名で市販されている。

【0037】他の適当な低塩基度架橋剤としては、ヒドロキシ化合物、特に、フェニル基、または少なくとも1個のヒドロキシ基もしくは $C_{1-8}$ ヒドロキシアルキル置換基のようなヒドロキシアルキル置換基を持つ芳香族類のような多官能化合物が挙げられる。フェノール化合物としては、ジメタノールフェノール ( $C_6H_3(CH_2OH)_2OH$ )、および隣接する (環の1-2の位置の原子) ヒドロキシ基およびヒドロキシアルキル基の置換基を持つ他の化合物、特に少なくとも1個のメタノールまたは他のヒドロキシアルキル置換基及びヒドロキシアルキル置換基に隣接する少なくとも1個のヒドロキシ基を持つフェニル基または他の芳香族化合物が一般的に好ましい。

【0038】ARCコーティング層を硬化させる間、該グリコウリル化合物の反応に対し触媒または促進作用を引き起こすために、本発明の架橋型反射防止組成物は、好ましくは、さらに酸または酸発生剤化合物を含有する。好ましくは、光分解または熱処理時に酸を発生する酸発生化合物が使用される。好ましくは、酸発生剤として、熱酸発生剤、すなわち、熱処理時に酸を発生する化合物が使用される。2, 4, 4', 6'-テトラプロモシクロヘキサジエノン、ベンゾイントシレート、ニトロベンジルトシレート、特に4-ニトロベンジルトシレートおよび他の有機スルホン酸のアルキルエステルのような種々の公知の熱酸発生剤が好適に使用される。活性化時にスルホン酸を発生する化合物が一般的に好適である。典型的には熱酸発生剤は、反射防止組成物の全乾燥成分の約0.5~15重量パーセント、より好ましくは全乾燥成分の約2重量パーセントの濃度で反射防止組成物の中に存在する。熱酸発生剤の代りまたは追加として、光酸発生剤が酸発生剤として使用でき、ARCコーティング層ブランケットは、上塗りされたフォトレジスト組成物の塗布前に活性化照射光に露光される。

【0039】また、むしろ酸発生剤の代りに、酸を本発明の架橋型ARCの中へ単に配合する場合があります、特に、ARCの使用前に酸が組成物成分の望ましくない反応を促進しないように、硬化させるのに酸の存在下で加熱する必要があるARC類の場合に使用される。好適な酸としては、例えば、トルエンスルホン酸、スルホン酸、トリフリック酸 (triflic acid) 等のスルホン酸類のような強酸、またはそれらの混合物が挙げられる。

【0040】本発明は、目的とするフォトレジスト組成物との使用の過程で著しい架橋が起こらない反射防止組成物も含む。そのような非架橋型の反射防止組成物は、架橋反応を誘起または促進させるための架橋剤成分または酸あるいは熱酸発生剤を含む必要がない。言い換えれば、そのような非架橋型の反射防止組成物は、一般的には架橋反応を促進させるための架橋剤成分および/または酸供給源を本質的に (すなわち約1または2重量パーセント未満) または完全に含まない。

【0041】また、本発明の反射防止組成物は、好ましくは、上塗りされたフォトレジスト層の望ましくないノッチング (notching) またはフーチング (footing) を十分抑制または実質的に防止する量で好適に用いられる1種以上の光酸発生剤 (すなわち、「PAG」) を含む。本発明のこの態様において、光酸発生剤は、架橋反応を促進させるための酸供給源としては使用されず、従って、好ましくは、光酸発生剤は、反射防止組成物 (架橋型ARCの場合) の架橋の過程で実質的に活性化されない。特に、熱的に架橋される反射防止組成物に関しては、反射防止組成物PAGは、該PAGが、上塗りされたフォトレジスト層のその次の露光過



程で活性化されて酸を発生するように、架橋反応条件に対して実質的に安定であるべきである。特に、好ましいPAGは、約140℃または150℃～190℃の温度に5分から30分またはそれ以上露光させた時に、実質的に分解ないしは劣化しない。

【0042】一般的に、本発明のARC類に用いられるような好ましい光酸発生剤としては、例えば、ジ(4-tert-ブチルフェニル)ヨードニウム ペルフルオロオクタンスルホネートなどのオニウム塩、1, 1-ビス[p-クロロフェニル]-2, 2, 2-トリクロロエタンのようなハロゲン化非イオン系の光酸発生剤、およびフォトレジスト組成物で使用するために本明細書に開示されている他の光酸発生剤が挙げられる。少なくとも本発明のいくつかの反射防止組成物に対しては、界面活性剤として作用し、反射防止組成物/レジスト塗布層の界面に近い、反射防止組成物層の上部近くに集合する、反射防止組成物用の光酸発生剤が好ましい。従って、例えば、そのような好ましいPAG類としては、4個以上の炭素、好ましくは6個～15個の炭素、または1個または好ましくは2個以上のフッ素置換基を持つC<sub>1</sub>～C<sub>15</sub>アルキルまたはC<sub>2</sub>～C<sub>15</sub>アルケニルのようなフッ素化された基を持つ、置換または非置換のアルキル基または脂環式基等の長鎖脂肪族基が挙げられる。

【0043】本発明の反射防止組成物用の特に好ましい光酸発生剤は、200nm未満、特に193nmの照射光で露光した時に活性化され、その結果、反射防止組成物は、193nmの光で画像形成される上塗りされたフォトレジストと共に効果的に使用される。反射防止組成物の光酸発生剤とフォトレジスト組成物の光酸発生剤は、同一露光波長で活性化されることが望ましい。また、フォトレジスト組成物および/または反射防止組成物に配合される増感剤は、反射防止およびフォトレジスト組成物の両方の光酸発生剤を、単一露光波長により確実に活性化するために使用される。

【0044】さらに好ましくは、本発明の反射防止組成物はフォトレジスト組成物と共に使用され、その場合は、反射防止組成物の光活性化化合物とフォトレジスト組成物の光活性化化合物が、フォトレジスト層の照射過程で、活性化照射への露光時に同一またはほぼ同一の酸化化合物(光生成物)、すなわち、好ましくは類似の拡散特性と酸強度を持つ光生成物、を発生する。反射防止組成物とレジストのそれぞれの光酸生成物(photoacid products)のそのようなマッチングにより、上塗りされたレジストのレリーフ画像の解像度がさらに向上することが見いだされている。ここで、本発明の「ほぼ同一の」反射防止組成物とレジストの光酸生成物に関して、それらは、2つの光生成物のpK<sub>a</sub>値(25℃で測定)の差が約2または2.5以下であり、好ましくは2つの光生成物のpK<sub>a</sub>値の差が約1ないし1.5以下であり、さらに好ましくは2つの光生成物のpK<sub>a</sub>

値の差が約0.75以下であることを意味する。さらに好ましくは、そのような「ほぼ同一の」反射防止組成物とレジストの光酸生成物の分子量の違いは、好ましくは約40パーセント以下、より好ましくは約20パーセント以下、さらに好ましくは約15パーセント以下である。また、さらに、反射防止組成物とレジストの光生成物が、例えば両光生成物がスルホン酸、または両者がHBr等のハロ酸類であるように、互いに同じクラスの酸であることが好ましい。好適なPAGの量は非常に広く変化させることができ、経験的に容易に決められる。一般的に、本発明の1種またはそれ以上のPAGは、反射防止組成物の全重量に対して約0.25から5重量パーセントまたはそれ以下の量で好適に使用できる。典型的な使用量については後述の実施例を参照されたい。また、本発明の反射防止組成物のPAGの特に好ましい量は、反射防止組成物と共に使用されるフォトレジストの特性と加工条件によって変えてよい。例えば、もしフォトレジストの光酸発生剤が比較強い酸光生成物を生成し、フォトレジストが比較的低温で露光後ベーク(PEB)される場合、反射防止組成物の光酸生成物は、そのような低いPEB温度ではより熱分解しにくいいため、反射防止組成物中での有効濃度は比較的高くなる。従って、その反射防止組成物は、比較的低濃度の光酸発生剤を使用して効果的に配合することができる。逆に、もし、フォトレジストが比較的高温で露光後ベーク(PEB)される場合、反射防止組成物の光酸生成物の一部がより熱分解されやすくなる。そのような場合、光生成物の有効濃度を確保し、望ましくないフーチング(footing)の低減を最大にするために、比較的高濃度の光酸発生剤が反射防止組成物に配合される。

【0045】本発明の反射防止組成物は、また、上塗りされたフォトレジスト層を露光するのに使用する照射光を吸収する追加の染料化合物を含んでもよい。必要に応じて使用する他の添加剤には、表面平滑剤が挙げられ、例えばユニオンカーバイド社(Union Carbide)からシルウエット(Silwet)7604の商品名で市販されている平滑剤、またはスリーエム社(3M)から市販されている界面活性剤FC430がある。そのような界面活性剤/表面平滑剤が好ましい。好ましい界面活性剤の濃度は固形分で0.5～15パーセント、より好ましくは固形分で0.7～1.0パーセントである。後述の実施例51～55を参照されたい。

【0046】液状コーティング組成物を作るには、反射防止組成物の成分を好適な溶媒に溶解させるが、その溶媒としては、例えば乳酸エチル、または、2-メトキシエチルエーテル(ジグリム)、エチレングリコールモノメチルエーテルおよびプロピレングリコールモノメチルエーテルのような少なくとも1種のグリコールエーテル類;メトキシブタノール、エトキシブタノール、メトキシプロパノールおよびエトキシプロパノールのようなエ

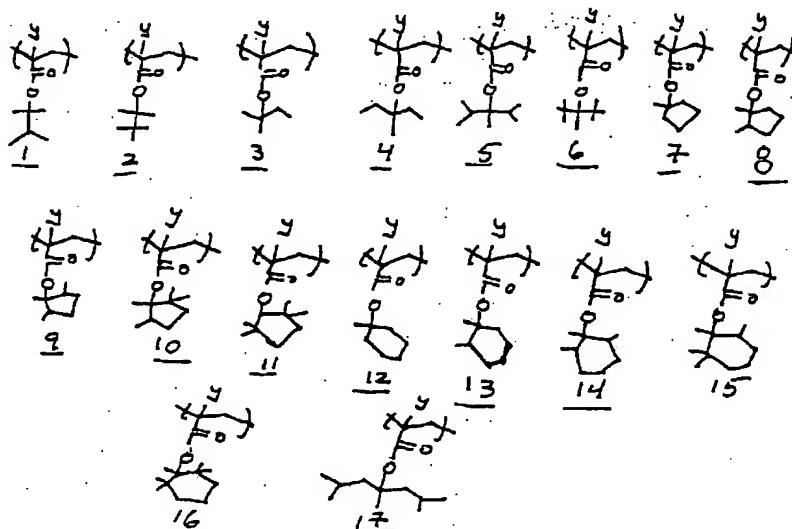
ーテル部分とヒドロキシ部分との両者を持つ溶媒；メチルセルソルブアセタート、エチルセルソルブアセタート、プロピレングリコールモノメチルエーテルアセタート、ジプロピレングリコールモノメチルエーテルアセタートのようなエステル類；並びに二塩基酸エステル、炭酸プロピレンおよびガンマーブチロラクトンのような他の溶媒である。溶媒中の乾燥成分の濃度は、塗布方法のようないくつかの因子によって決まる。一般的に、反射防止組成物の固形分量は、反射防止組成物の全量の約0.5～20重量パーセントで、好ましくは反射防止組成物の全量の約2～10重量パーセントまで変化する。

【0047】ポジ型及びネガ型の光酸発生組成物を含めて、種々のフォトレジスト組成物が、本発明の反射防止組成物と共に使用できる。好ましくは、本発明のARCは、化学増幅ポジ型レジスト組成物と共に使用される。本発明のARCと共に使用されるフォトレジストは、一般的に樹脂バインダーおよび光活性成分を含有する。

【0048】本発明のARCと共に使用される好ましいフォトレジストは、200nm未満、特に193nmの波長で画像形成されるように設計される。本発明のARCと共に使用される好ましいレジスト組成物は、1998年8月28日付にて提出された本出願人による米国特許出願番号第09/143,462号に開示されている。本発明のARCと共に使用される、特に好ましいレジスト樹脂バインダーは、次式の構造1から17の懸架したエステルのような、5個以上の炭素の非環状または単一環のアルキル基と、2個以上の二級炭素または三級炭素ラジカルを含有する、光酸感受性の懸架したエステル繰り返し単位を持つ。式中に示された置換基Yは、好ましくは水素またはメチル、より好ましくはメチルである。

【0049】

【化10】



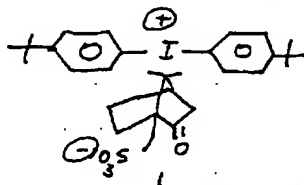
【0050】また、レジスト樹脂バインダー成分としてのポリマーは、懸架したシアノ基と無水イタコン酸基等の他の単位を持ってもよい。好ましくは、無水イタコン酸部分はポリマー主鎖に直接懸架する、すなわち該部分は、ポリマー結合基と無水イタコン酸基の間に介在するアルキレン基、アリール基または他の基を持たずに、ポリマー結合基に直接懸架する。一方、シアノ基は好ましくはポリマー主鎖に直接懸架するが、結合基がシアノ基とポリマー結合基の間に介在してもよい。

【0051】本発明のレジストの樹脂バインダーに使用されるポリマーは、所望ならばさらにフォトレジストの水系現像性に寄与する基などの単位を含有してよい。例えば、水系現像性に寄与する好ましいポリマー基としては、アクリル酸、メタクリル酸、メタクリル酸-2-ヒ

ドロキシエチル、または他のモノマーの重合により得られるようなカルボキシ部分またはヒドロキシ部分が挙げられる。他の好ましいポリマー単位としては、例えば、メタクリル酸-2-アダマンチル-2-メチル、メタクリル酸イソボルニルなどのビニル脂環式基、または、メタクリル酸-t-ブチルのような非環状アルキル基等の重合により得られる単位が含まれる。一般的に、本発明の化学増幅フォトレジストに使用する好ましい酸感受性(acid labile)ポリマーは、メタクリル酸イソボルニル、メタクリロニトリル、無水イタコン酸、メタクリル酸、メタクリル酸-t-ブチル、メタクリル酸-2-メチル-2-アダマンチルまたはメタクリル酸-2,3-ジメチル-2-ブチルのモノマーの1個以上の重合単位を持つ。

【0052】本発明のARCと共に使用される好適な樹脂の光酸発生剤化合物としては、本発明に引用記載されている米国特許第4,442,197号、第4,603,101号および第4,624,912号に開示されているようなオニウム塩、サッカレー等(Thackeray, et al.)の米国特許第5,128,232号に開示されているハロゲン化光活性化化合物のような非イオン系有機光活性化化合物、並びにスルホン化エステルおよびスルホンルオキシケトンを含めたスルホナート光酸発生剤などが挙げられる。ベンゾイントシレート、*t*-ブチルフェニルアルファー(*p*-トルエンスルホンルオキシ)-アセタートおよび*t*-ブチルアルファー(*p*-トルエンスルホンルオキシ)-アセタートを含む好適なスルホナートPAGの開示については、「ジャーナル オブ フォトポリマー サイエンス アンド テクノロジー」(J. of Photopolymer Science and Technology, 4(3):337-340, 1991)を参照されたい。好ましいスルホナートPAGはシンタ(Sinta, et al.)の米国特許第5,344,742号にも開示されている。

【0053】本発明のARCと共に使用される好適なフ



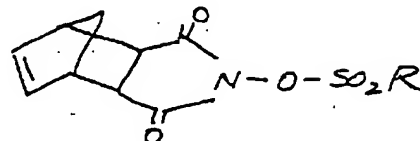
【0058】このようなスルホナート化合物は、上記PAG1の合成を詳細に記しているヨーロッパ特許出願第961181112号(公告番号0783136号)に開示されているように調製される。概略を述べると、PAG1は、ヨウ素酸カリウム、*t*-ブチルベンゼンおよび無水酢酸の混合物に硫酸を滴下し、氷浴で冷却しながら反応させて調製される。次いで、反応混合物を室温で約22時間攪拌し、水を加えて約5~10℃まで冷却し、次いでヘキサンで洗浄する。その後、ジアリールヨードニウム・硫酸水素塩の水溶液を約5~10℃まで冷却してショウノウスルホン酸を添加し、さらに水酸化アンモニウムで中和する。

【0059】また、上記のショウノウスルホナート基とペルフルオロオクタンスルホナート基以外のアニオンと錯体を形成した前記2種のヨードニウム化合物も好適である。特に、好ましいアニオンとしては、式 $RSO_3^-$ で示されるものが挙げられる。式中、Rは、アダマンタン、アルキル(例えば $C_{1-12}$ アルキル)及びペルフルオロ( $C_{1-12}$ アルキル)などの他のペルフルオロアルキル、特に、ペルフルオロブタンスルホナート等である。

フトレジスト用PAG類としては、次式の化合物のようなイミドスルホナート類が挙げられる。

【0054】

【化11】

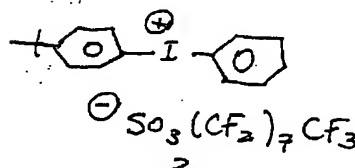


【0055】(式中、Rは、ショウノウ、アダマンタン、アルキル(例えば $C_{1-12}$ アルキル)およびペルフルオロ( $C_{1-12}$ アルキル)などのペルフルオロアルキル、特に、ペルフルオロオクタンスルホナート、ペルフルオロノナンスルホナート等である。特に好ましいPAGは、N-[ (ペルフルオロオクタンスルホンルオキシ)-5-ノルボルネン-2,3-ジカルボキシイミドである。)

【0056】また、本発明のARCと共に使用される樹脂として、次式のPAG1とPAG2も好適である。

【0057】

【化12】



【0060】他の公知のPAGもまた、本発明に従って使用される樹脂の中に使用できる。193nmでの画像形成のために、一般的に好ましいのは、レジストの透明性を高めるため、前述のイミドスルホナートのように芳香族基を持たないPAGである。

【0061】所望ならば、本発明の樹脂の好ましい添加剤としては、添加塩基、特に、現像したレジストレイフ画像の解像度を向上させるテトラブチルアンモニウムヒドロキッド(TBAH)、または乳酸テトラブチルアンモニウムが挙げられる。193nmで画像形成させるレジストに対して、好ましい添加塩基は、ジアゾビスクロウンデカンまたはジアゾビスクロノネンのようなヒンダードアミンである。添加塩基は、例えば全固形分の約0.03~5重量パーセントの比較的小量が好適に使用される。

【0062】本発明のフトレジストは、また、所望ならば他の物質も含有することができる。例えば、必要に応じた他の添加剤として、条線防止剤、可塑剤、増速剤等が挙げられる。例えば、レジスト乾燥成分の全重量の約5~30重量パーセントの量のような比較的高濃度で存在することがある充填剤や染料を除いて、このような

必要に応じて使用される添加剤は、フォトレジスト組成物に低濃度で存在するのが普通である。

【0063】好適なグリコウリルのような低塩基度架橋剤を含有する本発明のARCは、トリフリック酸、スルホン酸ショウノウもしくは他のスルホン酸、または約2以下の $pK_a$ （25℃）を持つ他の酸のような強酸光生成物を露光時に発生するフォトレジストと用いると特に有用である。理論に縛られることなく、より塩基性の架橋剤を含む同類のARCと比べ、レジストから移動してARC層の中に残る光発生型強酸がかなり少ないことから、本発明のARC類は、そのような強酸レジストと共に用いると特に有効であると考えられる。即ち、本発明の低塩基度架橋剤は、より塩基性のARC架橋剤と比べ、上塗りされたレジスト層の光発生型強酸との結合の程度が少ない。この結果、レジスト層から酸の消失は減り、潜在的フーチング（footing）のような解像度の問題は減少するか避けられる。

【0064】使用にあたっては、本発明の反射防止組成物は、スピニングのような種々の方法のいずれかによって基板へ塗布層として適用される。反射防止組成物は、通常約0.02と0.5 $\mu m$ の間の乾燥層の厚さ、好ましくは約0.04と0.20 $\mu m$ の間の乾燥層の厚さで基板に適用される。基板は、フォトレジストに関連するプロセスにおいて従来から使用されているいずれの基板でも好適である。例えば、該基板としては、シリコン、二酸化シリコン、またはアルミニウム-酸化アルミニウムのマイクロ電子ウエハー等が可能である。ヒ化ガリウム、セラミック、石英、または銅基板も使用してよい。液晶ディスプレイ、または、例えば、ガラス基板、インジウム酸化錫コーティング基板等の、平板パネルディスプレイ用に使用される基板も使用される。

【0065】好ましくは、フォトレジスト組成物がARC上に塗布される前に反射防止性層を硬化するのがよい。硬化条件は、ARC成分によって変化する。従って、この組成物が酸または酸発生剤を含まない場合は、硬化温度及び条件は、酸または酸発生剤化合物を含む組成物の場合よりも厳しい。代表的な硬化条件は、約120℃～225℃で約0.5～40分間である。ARCコーティング層を、アルカリ性現像水溶液だけでなくフォトレジスト溶媒にも実質的に不溶化させる硬化条件が好ましい。

【0066】このような硬化の後に、フォトレジストをARCの表面に塗布する。ARCの塗布と同様に、回転、浸漬、メニスカス（meniscus）またはロール塗布によるような通常のいずれの手段によってもフォトレジストを塗布できる。塗布の後は、一般的にフォトレジストコーティング層を加熱によって乾燥して、好ましくはレジスト層が非粘着性になるまで溶媒を除去する。最適には、ARC層とフォトレジスト層が本質的に相互に混じり合わないようにするべきである。

【0067】次に、従来の方法で、マスクを通して活性化照射でレジスト層に画像を形成させる。レジスト系の光活性成分を効果的に活性化するために十分な露光エネルギーによって、レジストコーティング層にパターン化された画像が形成される。より詳しくは、露光エネルギーは、露光機器によるが、一般的に約3から300mJ/cm<sup>2</sup>の範囲である。コーティング層の露光された領域と露光されない領域の間の溶解度の差を作り出し、またはその差を大きくにするためには、露光されたレジスト層に露光後ベーキングを施してもよい。例えば、ネガ型の酸硬化型フォトレジストは、酸促進型架橋反応を誘起するために一般的に露光後の加熱を必要とし、一方、多くの化学増幅型ポジ型レジストは酸促進型脱保護反応を行うために露光後の加熱を必要とする。一般的に、露光後のベーキング条件としては、約50℃以上の温度、より詳しくは約50℃～160℃の範囲の温度が挙げられる。

【0068】次いで、露光されたレジスト被覆層は現像されるが、テトラブチルアンモニウムヒドロキシドの例のような有機アルカリ、または、水酸化ナトリウム、水酸化カリウム、炭酸ナトリウム、炭酸水素ナトリウム、ケイ酸ナトリウム、メタケイ酸ナトリウム、アンモニア水等を例とする無機アルカリのような水性現像液を用いるのが好ましい。別の方法として、有機現像液を使用できる。一般的に、現像は当業者に良く知られている方法による。

【0069】次に、現像された基板はフォトレジストの露出された基板領域に、選択的加工、例えば当業者に公知の手順に従って、フォトレジストの露出された基板領域を化学的にエッチングまたはメッキすることができ。好適なエッチング剤としては、フッ化水素酸エッチング溶液、および酸素プラズマエッチング剤のようなプラズマガスエッチング剤が挙げられる。プラズマガスエッチング剤は架橋されたハレーション防止コーティング層を除去する。

【0070】

【実施例】本発明で述べる全ての文献は、本発明の中で参照している。以下の実施例は本発明を例示するもので、限定するものではない。

【0071】実施例 1-3： ポリマーの合成  
実施例 1： モル比が30：38：32である、スチレン、メタクリル酸-2-ヒドロキシエチルおよびメタクリル酸メチルのモノマーから成る3元コポリマーを以下の手順により合成した。上部攪拌機、凝縮器、および窒素導入口を取り付けた5Lの三口丸底フラスコの中で、モノマー（アルドリッチ社製の純度99%のスチレン169.79g；ロームアンドハース社製の「ロクリル400（Rocryl 400）」のメタクリル酸-2-ヒドロキシエチル269.10g；およびロームアンドハース社製のメタクリル酸メチル173.97g）を

2, 375 gのTHFに溶解した。反応溶液に窒素を20分間流して脱ガスを行った。溶液にデュボン社製の開始剤Vaz 52を11.63 g加え、加熱環流(65-67℃)を行いながらこの温度に15時間保った。反応溶液を室温に冷却した後、MTBE/シクロヘキサン(容積/容積 1/1)12 L中に沈殿させた。ポリマーを真空ろ過により収集し、50℃で48時間真空中で乾燥した。収率は68%で、その後の分析の結果残存モノマーは2.4重量%、Tg=92℃、Td=239℃であることが分かった。モノマーのモル濃度の合計に対するパゾ52開始剤のモル濃度の割合は0.72%であった。ゲル浸透クロマトグラフィー(gel permeation chromatography)による分子量解析の結果、Mw=22,416、Mn=10,031であることが分かった。

【0072】実施例 2-3: 投入モノマー量のモル%を下記に従って変更した以外は実施例1の手順と同様にして、スチレン:メタクリル酸-2-ヒドロキシエチル:メタクリル酸メチルの別の3元コポリマーを合成した。

実施例 2: モル%の比率12:38:50で合成したポリマー。沈殿溶剤としてt-ブチルメチルエーテル(5,000 mL)を用いた。収量は168 g(理論値の84%)であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=19,612、Mn=10,434であり、その後の分析の結果Tg=76℃、そしてTd=201℃であることが分かった。

【0073】実施例 3: モル%比18:38:44のスチレン、メタクリル酸-2-ヒドロキシエチルおよびメタクリル酸メチルモノマーより成る3元コポリマー。沈殿溶剤としてヘキサン(4,500 mL)を用いた。収量は68 g(理論値の79%)であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=22,712、Mn=11,564であり、その後の分析の結果Tg=107℃であることが分かった。

【0074】実施例 4: 実施例1の手順に従って、0.36モル%の開始剤Vaz 52を用い、モノマーのモル%比30:38:32でスチレン:メタクリル酸-2-ヒドロキシエチル:メタクリル酸メチルの3元コポリマーを合成した。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=54,502、Mn=22,495であった。

【0075】実施例 5: 実施例1の手順に従って、0.72モル%の開始剤Vaz 52を用い、モル%比30:38:31:1でスチレン:メタクリル酸-2-ヒドロ:メタクリル酸メチル:メタクリル酸-n-ブチルの4元コポリマーを合成した。ゲル浸透クロマトグラ

フィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=22,646、Mn=10,307であり、その後の分析の結果Tg=74℃、Td=331℃であることが分かった。

【0076】実施例 6: 実施例1の手順に従って、0.36モル%の開始剤Vaz 52を用い、モル%比18:38:44で4-アセトキシスチレン:メタクリル酸-2-ヒドロキシエチル:メタクリル酸メチルの3元コポリマーを合成した。ポリマー収率は84%であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=73,888、Mn=29,973であり、その後の分析の結果Tg=74℃、Td=247℃であることが分かった。

【0077】実施例 7: 実施例1の手順に従って、0.36モル%の開始剤Vaz 52を用い、モル%比30:38:32でメタクリル酸フェニル:メタクリル酸-2-ヒドロキシエチル:メタクリル酸メチルの3元コポリマーを合成した。収率は94%であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=111,039、Mn=26,866であり、その後の分析の結果Tg=91℃、Td=242℃であることが分かった。

【0078】実施例 8: 実施例1の手順に従って、0.91モル%の開始剤Vaz 52を用い、モル%比18:38:44でメタクリル酸ベンジル:メタクリル酸-2-ヒドロキシエチル:メタクリル酸メチルの3元コポリマーを合成した。ポリマー収率は99%であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=21,614、Mn=11,379であった。

【0079】実施例 9: 実施例1の手順に従って、0.91モル%の開始剤(パゾ52)を用い、モル%比18:38:44でメタクリル酸-2-フェニルエチル:メタクリル酸-2-ヒドロキシ:メタクリル酸メチルの3元コポリマーを合成した。ポリマー収率は98%であった。ゲル浸透クロマトグラフィーによる分子量解析の結果は、ポリスチレンの標準サンプルとの相対値でMw=29,008、Mn=15,956であった。

【0080】実施例 10: 以下の手順に従って、実施例1のポリマーを用いて反射防止コーティング(ARC)組成物を調製した。実施例1のポリマー1.2175 g、テトラメトキシメチルグリコルリル(アメリカンシアナミド社製)0.225 g、p-トルエンスルホン酸0.0075 g、FC-430(3M社製)0.0135 g、ジ(4-t-ブチルフェニル)ヨードニウムペルフルオロオクタンスルホネート(ダイケム社製)0.0965 gおよびプロピレングリコールモノメチルエーテルアルコール(「Dowanol PM」、ダウ社製)48.44 gを秤量して100 mLの瓶に入

れ、ローラーの上に置いて溶解を促進した。溶解した後0.1 $\mu$ mまたは0.2 $\mu$ mのテフロンフィルターを通してARC組成物をろ過し、清浄な瓶に入れた。

【0081】実施例 11： 以下の手順に従って、実施例1のポリマーを用いて反射防止コーティング（ARC）組成物を調製した。実施例1のポリマー1.2175g、テトラメトキシメチルグリコルリル（アメリカンシアナミド社製）0.150g、ヘキサメトキシメラミン混合物（「Cymel 303」）0.075g、p-トルエンスルホン酸0.0075g、FC-430（3M社製）0.0135g、ジ（4-*t*-ブチルフェニル）ヨードニウム ペルフルオロオクタンスルホナート（ダイケム社製）0.0965gおよびプロピレングリコール モノメチルエーテルアルコール（「Dowanol PM」、ダウ社製）48.44gを秤量して100mLの瓶に入れ、ローラーの上に置いて溶解を促進した。溶解した後0.1 $\mu$ mまたは0.2 $\mu$ mのテフロンフィルターを通してARC組成物をろ過し、清浄な瓶に入れた。

【0082】実施例 12： 以下の手順に従って、実施例1のポリマーを用いて反射防止コーティング（ARC）組成物を調製した。実施例1のポリマー4.571g、テトラメトキシメチルグリコルリル（アメリカンシアナミド社製）0.8438g、p-ニトロベンジルトシレート0.0281g、FC-430（3M社製）0.0450g、ジ（4-*t*-ブチルフェニル）ヨード

ニウム ペルフルオロオクタンスルホナート（ダイケム社製）0.1371gおよびプロピレングリコールモノメチルエーテルアルコール（「Dowanol PM」、ダウ社製）48.44gを秤量して500mLの瓶に入れ、ローラーの上に置いて溶解を促進した。溶解した後0.1 $\mu$ mまたは0.2 $\mu$ mのテフロンフィルターを通してARC組成物をろ過し、清浄な瓶に入れた。

【0083】実施例 13： 以下の手順に従って、実施例1のポリマーを用いて反射防止コーティング（ARC）組成物を調製した。実施例1のポリマー1.314g、テトラメトキシメチルグリコルリル（アメリカンシアナミド社製）0.225g、p-トルエンスルホン酸0.0075g、FC-430（3M社製）0.0135gおよびプロピレングリコール モノメチルエーテルアルコール（「Dowanol PM」、ダウ社製）48.44gを秤量して100mLの瓶に入れ、ローラーの上に置いて溶解を促進した。溶解した後0.1 $\mu$ mまたは0.2 $\mu$ mのテフロンフィルターを用いてARC組成物をろ過し、清浄な瓶に入れた。

【0084】実施例 14-18： p-トルエンスルホン酸およびテトラメトキシメチルグリコルリルの量を変更した以外は、実施例13と非常に類似した手順と組成を用いて反射防止組成物を調製した。組成物の中の固形分の全量に対する、これら2つの成分の重量パーセントを表1に示す。

【0085】

表 1： ARC 組成物

実施例	テトラメトキシメチルグリコルリル	p-トルエンスルホン酸
	固形分重量%	固形分重量%
14	12	0.1
15	18	0.1
16	15	0.3
17	12	0.5
18	18	0.5

【0086】実施例 19-23 FC430の量を変更した以外は、実施例13と非常に類似した手順と組成を用いて反射防止組成物を調製した。組成物の中の固形分の全量に対する、この成分の重量パーセントを表2に示す。

【0087】

表 2： ARC 組成物

実施例	FC430 固形分重量%
19	0.2
20	0.5
21	0.8
22	1.1
23	2.0

【0088】実施例 24-25： 組成物中の各成分の重量を以下のようにし、実施例13と非常に類似した手順と組成を用いて反射防止組成物を調製した： ポリマー0.6102g、テトラメトキシメチルグリコリル（アメリカンシアナミド社製）0.1125g、p-トルエンスルホン酸0.0030g、FC-430（3M社製）0.0060g、ジ（4-tert-ブチルフェニル）ヨードニウム ペルフルオロオクタンスルホナート（ダイケム社製）0.0183gおよびプロピレングリコール モノメチルエーテルアルコール（「Dowanol PM」、ダウ社製）24.25g。これらの組成物を表3に記載する。

実施例	使用したポリマーの実施例
24	8
25	9

【0090】実施例 26-32： 組成物中の各成分の重量を以下のようにし、実施例13と非常に類似した手順と組成を用いて反射防止組成物を調製した： ポリマー0.974g、テトラメトキシメチルグリコリル（アメリカンシアナミド社製）0.180g、p-トルエンスルホン酸0.0060g、FC-430（3M社製）0.0108g、ジ（4-tert-ブチルフェニル）ヨードニウム ペルフルオロオクタンスルホナート（ダイケム社製）0.0292gおよびプロピレングリコール モノメチルエーテルアルコール（「Dowanol PM」、ダウ社製）38.80g。これらの組成物を

表4に記載する。

実施例	使用したポリマーの実施例
26	1
27	4
28	6
29	7
30	2
31	3
32	5

【0092】実施例 33-35： ARC組成物の光学テスト

ARC組成物を200mmのSiウエハー上にスピニングし、新型のFSIウエハー塗布ライン（wafer coating track）を用いて、非接触式150μm近接加熱板上で215℃で90秒間ベーキングを行った。ARC膜をウォーレン偏光解析型屈折率計（Wollem ellipsometer）（Lincoln NE）を用いて測定を行い、193nmにおける光学的な屈折率nおよびk（実際のおよび仮想の）を定量した。仮想の屈折率は膜の吸光度に関連している： ARC膜厚を最小化しながら膜の重なり反射率を最小化するためには、kの値は0.3以上である必要がある。最も望ましいkの値は、約0.4以上である。これらの値を表5に記載する。

【0093】

表5： 193nmで測定したARC組成物の光学パラメーター

実施例	実際の屈折率n	仮想の屈折率k
シップレーAR2 (シップレー社製)	1.70	0.10
33	1.73	0.216
34	1.74	0.295
35	1.77	0.40

【0094】これらのデータは、比較材料、すなわち、248nmにおいて使用する目的で設計され広く使用されている商業用ARC材料であるシップレーAR2が、193nmにおいて反射率を最小化するために望まれる値に比べて著しく低い仮想の屈折率を有していることを示す。これらのデータはまた、組成物30-32のk値がポリマー中のフェニル部分（このケースではスチレンモノマーを通じて導入された）が増加する程増大することを示す。本発明者らは、フェニル基は193nmにおける良好な発色団であり、ポリマー中のフェニル基の理想的な濃度を選択することにより、望ましい仮想の屈折率、kを得ることができると信じている。

【0095】実施例 36-40： ベーキング後のA

RCの不溶性の評価

ARC膜がコーティングおよびベーキング工程の間に硬化し、その結果その後のリソグラフィー（lithography）加工段階の中で、引き続きコーティングされるフォトリソレジストに対して非感受性になることが強く望まれる。本発明において、ベーキング中のARCの硬化は、ポリマーの化学的な酸触媒による架橋を通じて達成される。特に半導体製造において使用される最新の欠陥の無いリソグラフィー加工は、レジストのパターンとARCコーティング基板との界面に可能な限りスカム（scum）、残渣、およびフレア（flare）がなく、一方で優れた画像端部の鋭さを維持することを要求している。レジストのパターンはまた、リソグラフィー

工程の段階の間ARCに良く接着していなければならぬ。これらの要求を満たすために、本発明者らは、レジストと硬化したARC膜との相互の混ざり合いは、可能な限り最少化すべきであると信じる。いくつかの硬化したARC膜について、それらの代表的な、商業的に使用されているレジストコーティング用溶剤である乳酸エチルの中で、溶解または膨潤に対する感受性を持つかどうかを定量化することを検討した。そのため、ARC組成物をSi上にコーティングし、215℃で60秒ベーキ

ングを行って厚み60nmの膜を得た。膜厚はナノメトリクス(Nanometrics)215AFT膜厚測定器を用いて11個所で測定した。次いでARC塗布ウェハーを、乳酸エチル溶剤を入れたビーカーに60秒浸漬した。乳酸エチルを水ですすぎ落とした後、ウェハーを空気乾燥した。膜厚を同じ測定器を用いて同じ個所で測定し、厚みの変化を記録した。結果を表6に示す。

【0096】

表6： 乳酸エチル中60秒浸漬後のARC膜厚の変動

実施例	レジスト組成物	漬後の厚み変化(%)	コメント
36	14	44*減少	膜の変色
37	15	34*減少	膜の変色
38	16	0*	良好品質
39	17	0*	良好品質
40	18	0*	良好品質

\*：単位はオングストローム

【0097】実施例38-40は、組成物16、17および18が乳酸エチル溶剤中で溶解または膨潤のいずれにも非感受性であることを示す。この肯定的な結果は、これらの組成物が標準的なリソグラフィーによるパターン形成の間、レジストパターンとARC膜の間に結果として鮮明な界面を形成するであろうことを示唆する。実施例36-37は、レジスト溶剤の中でARCのいくつかの溶解を示しており、リソグラフィー加工が実施例38-40程良好ではなさそうであることを示唆している。組成物16-18は、トルエンスルホン酸の濃度がより低い(0.1%)実施例14および15に比べて、当初のARC組成物中により高い酸の濃度(0.3%-0.5%)を有していた。結果として、ARC組成物中における好ましい酸の濃度は0.1%より大きく、より好ましくは0.3%以上である。理論に拘らないが、より高い酸濃度はベーキング中のARC膜におけるより高い架橋密度をもたらす、溶剤の攻撃に対して膜をより非感受性にするに信じる。従って、少なくとも0.3%のトルエンスルホン酸の濃度が、以後のARC材料および組成物の評価に用いられた。

【0098】実施例41-42：ARCの性能評価に使用されるレジスト組成物  
パーフロロオクタンスルホネートノルボルネンジカルボキシイミド0.524g、ジ(4-tertブチルフェニル)ヨードニウムペルフルオロオクタンスルホネート

ト(DTBIPFOS)0.0449gおよびバインダーポリマーの組み合わせを、1,8-ジアザビシクロ[5,4,0]ウンデカ-7-エン(アルドリッチ社製、米国)0.0045g、シルウエット7604(Silwet7604、ダウコーニング社製、米国)0.0075gおよびプロピレングリコールメチルエーテルアセタート(ダウ社製、米国)43.5gを含む保存溶液の中に溶解することにより、リソグラフィーテストに好適なフォトレジスト組成物を調製した。DTBIPFOSの溶解を助長するために、この化合物を乳酸エチルの5%溶液としてレジスト組成物に加えた。溶解した後、0.1μmまたは0.2μmのテフロンフィルターを通してレジスト組成物をろ過し、清浄な瓶に入れた。

【0099】実施例41：記載したレジスト組成物に、メタクリル酸イソボルニル：メタクリル酸-tertブチル：メタクリル酸：メタクリロニトリル：無水イタコン酸の供給モル比を31：22：10：14：23にして得られたバインダーポリマーを使用した。以下の手順によりこのポリマーを調整した。無水イタコン酸12.54g、メタクリル酸-tertブチル15.20g、メタクリロニトリル4.58g、メタクリル酸4.28g、メタクリル酸イソボルニル33.57g、および100mLの無水のテトラヒドロフランを500mLのフラスコに入れた。全ての試薬の純度は少なくとも99%であった。フラスコには、磁気式攪拌棒、凝縮機、および注



加用ろうとが取り付けられた。反応に先立って、全ての成分を窒素ガスで20分間バージした。フリーラジカル開始剤Vazo 52、0.75gおよび無水のテトラヒドロフラン25mLを注加用ろうとに入れた。溶液を70℃に昇温し、次いで開始剤を20分間にわたって注加した。フラスコを70℃に14時間保ち、その後室温に冷却した。3Lのヘキサンの中で沈殿させ、ブフナーろうと(Buchner funnel)の中で乾燥してポリマーを得た。次いでそのポリマーを120mLのアセトン中に再溶解し、そして3Lのヘキサン中で再沈殿して、ブフナーろうと上に集めた。ポリマーを真空オープン中室温で一晩乾燥した。収量は49.96g(66%)であった。

【0100】実施例 42: 記載したレジスト組成物に、メタクリル酸イソボルニル:メタクリル酸-2,3-ジメチルブチル:メタクリル酸-tert-ブチル:メタクリル酸:メタクリロニトリル:無水イタコン酸の供給モル比を15:10:28:10:14:23にして得られたバインダーポリマーを使用した。以下の手順によりこのポリマーを調整した。実施例41と類似の手順によりこのポリマーを調整した。メタクリル酸-2,3-ジメチルブチルは、以下の手順により合成した。無水のテトラヒドロフラン180g、2,3-ジメチル-1-ブタノール40gおよびトリエチルアミン40.93gを、攪拌棒を入れ凝縮機を取り付けた500mLのフラスコにN<sub>2</sub>雰囲気下で入れた。これに精製したメタクリル酸クロリド40.927gを注加用ろうとから滴下しながら加えた。穏やかに加熱して反応を行った。24時間攪拌した後、回転式蒸発器を用いて溶液からテトラヒドロフランを蒸発し、100mLの酢酸エチルを加えた。次いでブフナーろうとを通して塩をろ別した。酢酸エチルは回転式蒸発器の使用により除去した。8インチのビグロウカラム(Vigreux column)、攪拌棒および数個の小さい沸石を備えた減圧蒸留筒を用意した。分別蒸留を実施して、6-7トールの圧力下で約80-87℃の沸点を有する画分として生成物19.8gを回収した。<sup>1</sup>H NMRを用いて構造と純度を確認した。

【0101】実施例 43-64: ARC組成物上のレジストのリソグラフィーによるパターン形成  
解像度の性能を評価するために、高圧断面走査型電子顕微鏡法を用いて焼き付けられた特性を検査した。1:1のピッチの格子画像における最小解像度は、マスク上に形成された1:1の160nmの線と160nmのスペースが、実際にそれぞれ実質的に160nmの寸法で測定されるような露光量を選択することにより、次いで清

浄に現像された実質的に所定の膜厚を保持した最小の線(full-thickness line)が、平滑な頂部を有し基板に残渣が残っていないことを測定することにより評価した。感光速度は、そのようなパターンを形成するのに必要な露光量で表す。感光速度は、ARC組成物が異なっても著しくは変わらないということが分かる。実施例41のレジスト組成物は約29mJ/cm<sup>2</sup>の感光速度を示し、実施例42のレジスト組成物は約24mJ/cm<sup>2</sup>の感光速度を示した。最新のウェハー加工装置(エフエスアイ アンド エスブイジー社(FSI and SVG Companies)製)の上で、150mmおよび200mmのシリコンウェハーの双方を使用してリソグラフィー加工を実施した。全ての加工は、実質的に塩基性汚染物質の無い(測定アミン/アンモニア5ppb以下)雰囲気中で行った。その後の加工に先立って、ウェハーにARC組成物を塗布した。約65nmの厚みを与えるように選択された好適な回転速度でARC膜をスピコートし、215℃でベーキングした。フォトレジストを約3,000rpmでウェハー上にスピコートし、非接触式150μm近接加熱板(proximity-gap plate)の上でベーキングを行い(塗布後硬化(PAB))、その後急速に室温に冷却して4,200オングストロームの膜厚を得た。次いでこの膜に、GCA0.60NA ArF(193nm)ウェハーステッパーの上で、部分コヒーレンス(coherence)設定0.70にて、解像度テストパターンを用いて露光を行った。その後直ちに、この膜を非接触式150μm近接加熱板の上でベーキングを行い(露光後硬化(PEB))、その後急速に室温に冷却した。その後直ちに、この膜を工業規格の60秒シングルバドル式工程(60 second track-single-puddle process)にて工業規格の0.26Nテトラメチルアンモニウムヒドロキシド現像液で現像した。

【0102】表7: ARC上のレジスト組成物のリソグラフィーテスト結果

Res LはEsにおける解像度を表す。PABおよびPEBは℃の単位で、そしてRes Lはnmの単位で表す。DUV-18Jは商業的に使用されているARC製品で、ミズーリ州のブリュワーサイエンス社(Brewer Sciences Incorporated)から市販されており、AR2はマサチューセッツ州のシップレー社(Shipley Company)から市販され商業的に使用されているARC製品である。

【0103】

実施例	ARC 実施例	レジスト 実施例	PAB	PEB	Res L	レジスト断面 コメント
44-比較	DUV18J	41	140	155	>160	スカム不良；フレア
45-比較	AR2	41	140	155	N/A	レジスト接着不良
46	10	41	140	155	150	エッジ鋭さ良好
47	11	41	140	155	150	エッジ鋭さ良好
48	12	41	140	155	150	エッジ鋭さ良好
49	13	42	140	150	140	エッジ鋭さ良好
50	16	41	140	155	150	僅かなスカム
51	19	41	140	155	150	僅かなスカム
52	20	41	140	155	150	極く僅かなスカム
53	21	41	140	155	150	エッジ鋭さ良好

【0104】

表7 (続き)

54	22	41	140	155	150	極く僅かな細り
55	23	41	140	155	150	僅かな細り
56-比較	24	41	140	155	160	フレアおよびスカム
57-比較	25	41	140	155	155	フレアおよびスカム
58	26	41	140	155	150	エッジ鋭さ良好
59	27	41	140	155	150	エッジ鋭さ良好
60	28	41	140	155	150	エッジ鋭さ良好
61	29	41	140	155	150	エッジ鋭さ良好
62	30	41	140	155	150	エッジ鋭さ良好
63	31	41	140	155	150	エッジ鋭さ良好
64	32	41	140	155	150	エッジ鋭さ良好

【0105】実施例17-32の考察

本発明の組成物は、半導体の製造用途に好適な著しく高性能のARC類をもたらすことができる。レジストパターンとARC下引き層との間の界面の品質は、より鮮明でより残渣が少なく、そしてARC組成物46-49、53および58-61の解像度は、従来のARC材料であるDUV-18JおよびAR2の解像度を上回っている。ARC組成物46-49、53および58-61の性能はまた、比較用の実施例56および57の性能を上回っている。組成物46-49、53および58-61の優れた性能はまた、ポリマーがポリマー鎖とフェニル発色団（例えば、実施例56におけるメタクリル酸フェニルや実施例57におけるメタクリル酸ベンジル）との間にアルキル介在グループ（alkyl spacer group）構造を持たない時最良の結果が得られる

【0106】実施例65：反射抑制のテスト

リソグラフィー工程の中でARCを使用する第一の目的は、レジストの「振動曲線」（“swing curve”）を最小化すること、すなわち、レジストの膜厚が変わるにつれて実測感光速度に見られる変動を最小化することである。反射抑制を評価するために、実施例44-64の工程と同様の工程によって実施例49のレジストを実施例13のARCの上でリソグラフィー的手法で加工した。ただし例外としてARC膜厚を82.5nmに保ち、そしてスピンコーティングの速度を変えることによりレジスト膜の厚みを400nmから500nmに変えた。感光速度としてパターン形成に要する露光量（E<sub>0</sub>）を測定した。そのデータを下記の表8に示す。

【0107】

表8： 実測したレジストの感光速度、E<sub>0</sub>対実施例13の

ARC上のレジスト膜厚

レジスト膜厚 (nm)	感光速度、E <sub>0</sub> (mJ/cm <sup>2</sup> )
402	7.8

4 1 2  
4 2 3  
4 2 9  
4 6 3  
4 7 1  
4 9 2

7. 7  
7. 5  
7. 5  
8. 0  
7. 9  
7. 8

【0108】実測された $E_0$ の変動における最大の変動幅は、 $8.0 - 7.5 = 0.5 \text{ mJ/cm}^2$ である。これは極めて小さい感光速度の変動であり、そして殆どの最新のリソグラフィ工程に対しても許容されるものである。この小さい値は、本発明の組成物が193 nmにおける露光の間、基板からの光の反射を抑制するのに有

効であることを示している。

【0109】本発明のこれまでの記載は単にそれを例示するためのものであり、以下の請求の範囲の中で説明するように、本発明の範囲または精神から離れることなしに、変更や修正を行い得るものである

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フロントページの続き

(71)出願人 596156668

455 Forest Street, Marlborough, MA 01752 U.S.A

(72)発明者 エドワード・ケイ・パベルチェク

アメリカ合衆国01775マサチューセッツ州  
ストウ オールド・ボルトン・ロード  
102

(72)発明者 ロジャー・エフ・シンタ

アメリカ合衆国01801マサチューセッツ州  
ウォバーン アンナ・ロード 9

(72)発明者 マニエル・ドゥキヤント

アメリカ合衆国02072マサチューセッツ州  
スタウトン アトキンソン・アベニュー  
59

(72)発明者 ロバート・エフ・ブラックスミス

アメリカ合衆国01452マサチューセッツ州  
ハッバードストン チコピー・ドライブ  
75

(72)発明者 ピーター・トレフォナス・サード

アメリカ合衆国02053マサチューセッツ州  
メドウェイ サマーヒル・ロード 40

【外国語明細書】

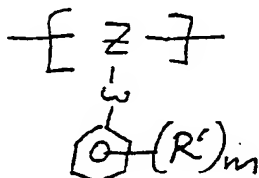
1. Title of Invention

Antireflective Coating Compositions

2. Claims

1. A method for forming a photoresist relief image comprising:
  - (a) applying on a substrate a layer of an antireflective composition that comprises a resin binder that has phenyl groups;
  - (b) curing the antireflective composition layer;
  - (c) applying a layer of a photoresist composition over the antireflective composition layer;
  - (d) exposing the photoresist layer to activating radiation and developing the exposed photoresist layer.
2. The method of claim 1 wherein the photoresist layer is exposed with activating radiation having a wavelength of below about 200 nm.
3. The method of claim 1 wherein the photoresist layer is exposed with activating radiation having a wavelength of about 193 nm.
4. The method of claim 1 wherein the phenyl groups are directly pendant from the resin backbone of the antireflective composition resin.
5. The method of claim 1 wherein the phenyl groups are pendant from the antireflective composition resin backbone and do not have any alkyl units interposed between the resin backbone and phenyl groups.

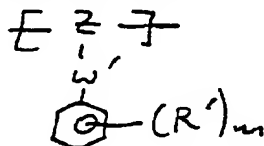
6. The method of claim 1 wherein the resin of the antireflective composition comprises units of the following Formula I:



I

where W is a chemical bond, an alkyl linkage, or an ester linkage;  
 each R' is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, ester, optionally substituted alkanoyl, optionally substituted carbocyclic aryl, or optionally substituted aralkyl;  
 m is an integer of from 0 to 5; and  
 each Z is independently a bridge group between polymer units.

7. The method of claim 1 wherein the resin of the antireflective composition comprises units of the following Formula IA:

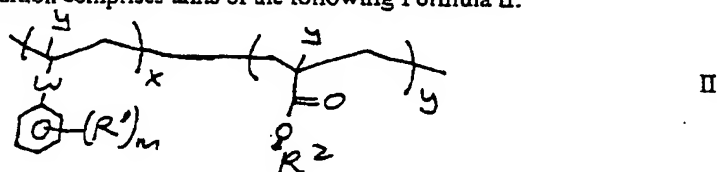


IA

where W' is a chemical bond or an ester linkage;  
 each R' is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, ester, optionally substituted alkanoyl, optionally substituted carbocyclic aryl, or optionally substituted aralkyl;  
 m is an integer of from 0 to 5; and  
 each Z is independently a bridge group between polymer units.

8. The method of claim 1 where in the antireflective composition resin is an acrylate resin.

9. The method of claim 1 wherein the resin of the antireflective composition comprises units of the following Formula II:



where W is a chemical bond, an alkyl linkage, or an ester linkage;

each R' is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, ester, optionally substituted alkanoyl, optionally substituted carbocyclic aryl, or optionally substituted aralkyl;

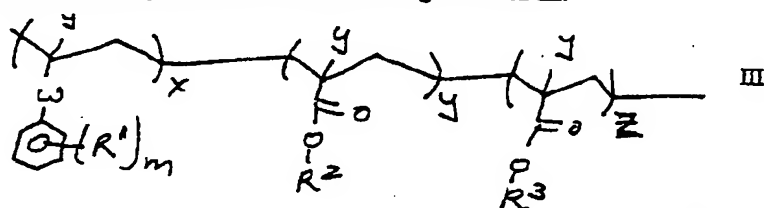
R<sup>2</sup> is optionally substituted alkyl or optionally substituted carbocyclic aryl;

each Y is independently hydrogen or optionally substituted C<sub>1-4</sub> alkyl; and

x and y are mole percents of the respective units in the resin.

10. The method of claim 9 wherein the R<sup>2</sup> contains a hydroxy group.

11. The method of claim 1 wherein the resin of the antireflective composition comprises units of the following Formula III:



where W is a chemical bond, an alkyl linkage, or an ester linkage;

each R' is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, ester, optionally substituted alkanoyl, optionally substituted carbocyclic aryl, or optionally substituted aralkyl;

R<sup>2</sup> and R<sup>3</sup> are each different and independently optionally substituted alkyl or optionally substituted carbocyclic aryl;

each Y is independently hydrogen or optionally substituted C<sub>1-6</sub> alkyl; and

x, y and z are mole percents of the respective units in the resin.

12. The method of claim 11 wherein at least one of the R<sup>2</sup> or R<sup>3</sup> substituent has a hydroxy group.

13. The method of claim 1 wherein the antireflective composition comprises a thermal acid generator compound.

14. The method of claim 1 wherein the antireflective composition is thermally cured prior to applying the photoresist composition layer.

15. The method of claim 1 wherein the antireflective composition comprises a photoacid generator, and the photoacid generator is not substantially activated until the exposing of the photoresist composition layer.

16. The method of claim 1 wherein the antireflective composition comprises a crosslinker material.

17. The method of claim 1 wherein the photoresist composition is a chemically amplified positive-acting photoresist.

18. A method for forming a photoresist relief image comprising:

(a) applying on a substrate a layer of an antireflective composition that comprises a resin binder that has phenyl groups;

(b) applying a layer of a photoresist composition over the antireflective composition layer;

(c) exposing the photoresist layer to activating radiation and developing the exposed photoresist layer.

19. The method of claim 18 wherein the photoresist layer is exposed with activating radiation having a wavelength of below about 200 nm.

20. The method of claim 18 wherein the phenyl groups are directly pendant from the resin backbone of the antireflective composition resin.

21. A coated substrate comprising:

a coated substrate having thereon

- 1) a coating layer of an antireflective composition that comprises a resin that has phenyl groups; and
- 2) a coating layer of a photoresist over the antireflective composition layer.

22. A bottom-layer antireflective composition for use with imaging an overcoated photoresist at sub-200 nm wavelengths, comprising a resin that has phenyl groups.



### 3. Detailed Description of Invention

#### BACKGROUND OF THE INVENTION

##### 1. Field of the Invention

The present invention relates to compositions that reduce reflection of exposing radiation from a substrate back into an overcoated photoresist layer. More particularly, the invention relates to antireflective coating compositions ("ARCs") that contain a resin binder components that effectively absorbs short-wavelength exposure radiation, including sub-200 nm radiation such as 193 nm radiation.

##### 2. Background

Photoresists are photosensitive films used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or crosslink in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions are known to the art and described by Deforest, *Photoresist Materials and Processes*, McGraw Hill Book Company, New York, ch. 2,

1975 and by Moreay, *Semiconductor Lithography, Principles, Practices and Materials*, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference for their teaching of photoresist compositions and methods of making and using the same.

A major use of photoresists is in semiconductor manufacture where an object is to convert a highly polished semiconductor slice, such as silicon or gallium arsenide, into a complex matrix of electron conducting paths, preferably of micron or submicron geometry, that perform circuit functions. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the more important steps in attaining high resolution photoresist images.

Reflection of activating radiation used to expose a photoresist often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce variations in the radiation intensity in the photoresist during exposure, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity. Variations in substrate topography also give rise to resolution-limiting reflection problems.

With recent trends towards high-density semiconductor devices, there is a movement in the industry to shorten the wavelength of exposure sources to deep ultraviolet (DUV) light (300 nm or less in wavelength), KrF excimer laser light (248.4 nm), ArF excimer laser light (193 nm), electron beams and soft x-rays. The use of shortened wavelengths of light for imaging a photoresist coating has generally resulted in increased reflection from the upper resist surface as well as the surface of the underlying substrate. Thus, the use of the shorter wavelengths has exacerbated the problems of reflection from a substrate surface.

Another approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer interposed between the substrate surface and the photoresist coating layer. See, for example, PCT Application WO 90/03598, EPO Application No. 0 639 941 A1 and U.S. Patent Nos. 4,910,122, 4,370,405 and 4,362,809, all incorporated herein by reference for their teaching of antireflective (antihalation) compositions and the use of the same. Such layers have also been referred to in the literature as antireflective layers or ARCs (antireflective compositions).

In Shipley Company's European Applications 542008A1 and 0813114A2 highly useful antihalation (antireflective) compositions are disclosed.

While it has been found that prior ARC compositions may be effective for many antireflective applications, prior compositions also may pose some potential performance limitations, particularly when used at short wavelength imaging applications.

It thus would be desirable to have new antireflective coating compositions. It would be particularly desirable to have new antireflective coating compositions that effectively absorb undesired reflections of short wavelength radiation, including sub-200 nm radiation such as 193 nm.

#### SUMMARY OF THE INVENTION

The present invention provides new light absorbing compositions suitable for use as an antireflective coating composition ("ARC"), particularly for short wavelength imaging applications, such as 193 nm imaging. The ARCs of the invention in general comprise a resin binder that effectively absorbs short wavelength exposure radiation to reduce reflections of same, and optionally comprise a crosslinker component.

Preferred resin binders of ARCs of the invention contain phenyl units, preferably pendant from a polymer backbone.

Particularly preferred ARC resin binders of the invention do not have any alkyl (e.g. optionally substituted  $(-\text{CH}_2-)_n$ , where  $n$  is 1 to about 6 or 8) units interposed between the polymer backbone and a pendant phenyl group. For example, preferred pendant groups include those provided by polymerization of optionally substituted styrene, optionally substituted isopropenyl styrene, optionally substituted phenyl acrylate, and optionally substituted phenyl methacrylate. As referred to herein, references to a phenyl group being "directly pendant" from a polymer backbone indicate that no alkyl or other groups are interposed between the polymer backbone and the phenyl group, such as provided by condensation of optionally substituted styrene or isopropenyl styrene units.

Nevertheless, while less preferred, the invention also includes ARCs having resin binders that have pendant phenyl groups where an alkyl (e.g. optionally substituted  $(-\text{CH}_2-)_n$ , where  $n$  is 1 to about 6 or 8) linkage is interposed between the backbone and the phenyl group, e.g. as may be provided by polymerization of 2-phenyl-1-ethyl methacrylate and the like.

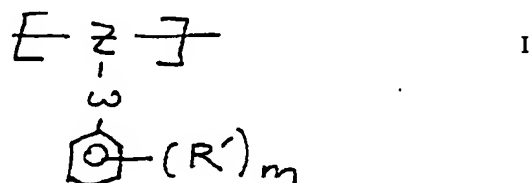
The antireflective composition resin binder with phenyl chromophore moieties suitably is a copolymer and is prepared by polymerizing two or more different monomers where at least one of the monomers includes a phenyl chromophore group. For example, preferred additional ARC resin units include those provided by polymerization of acrylate monomers, e.g. hydroxy acrylates such as 2-hydroxyethylmethacrylate, 2-hydroxyethylacrylate and the like;  $\text{C}_{1-12}$  acrylates such as methylmethacrylate, methylacrylate, butylmethacrylate, butylacrylate and the like. Acrylate resins that contain phenyl chromophore units are generally preferred for use in ARCs of the invention. For crosslinking ARCs of the invention, preferably the ARC resin has a hydroxy or other reactive moiety for promoting a curing reaction.

The invention further provides methods for forming a relief image and novel articles of manufacture comprising substrates coated with an ARC composition of the invention alone or in combination with a photoresist composition. Other aspects of the invention are disclosed *infra*.

#### DETAILED DESCRIPTION OF THE INVENTION

The resin binder component of the antireflective compositions of the invention are preferably used with short wavelength imaging systems and will effectively absorb sub-200 nm reflections, particularly 193 nm reflections.

In particular, preferred ARC resin binders of the invention have pendant phenyl groups. For example, preferred resins have phenyl units of the following Formula I:



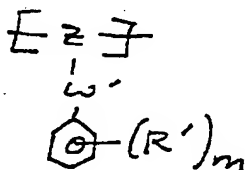
where W is a chemical bond, an alkyl linkage e.g. optionally substituted  $(-\text{CH}_2-)_n$  where n is from 1 to about 6 or 8), or an ester linkage (i.e.  $(\text{C}=\text{O})\text{O}$ );

each R' hydrogen or a non-hydrogen substituent such as halogen (F, Cl, Br or I); optionally substituted alkyl preferably having 1 to about 8 carbon atoms; optionally substituted alkoxy preferably having 1 to about 8 carbon atoms; optionally substituted ester such as  $-\text{C}(=\text{O})\text{OZ}$  where Z is  $\text{C}_{1-8}$  optionally substituted alkyl; optionally substituted alkanoyl such as  $\text{C}_{1-8}$  alkanoyl e.g. acyl and the like; optionally substituted carbocyclic aryl particularly phenyl; optionally substituted aralkyl particularly benzyl  $(-\text{CH}_2\text{C}_6\text{H}_5)$ ; and the like;

m is an integer of from 0 (where the pendent phenyl group is fully hydrogen substituted) to 5; and

Z is a bridge group between monomer units of the polymer, e.g. reactive moieties of monomer units such as carbon-carbon double bonds that are polymerized to provide e.g. optionally substituted alkylene, preferably C<sub>1-3</sub> alkylene optionally substituted by C<sub>1-4</sub> alkyl.

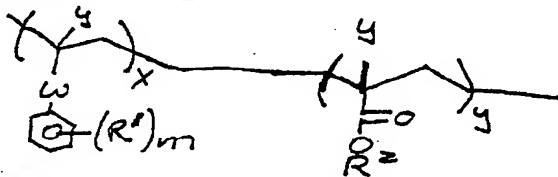
As discussed above, more preferred are resins that have pendant phenyl groups but without any alkyl (e.g. optionally substituted (-CH<sub>2</sub>-)<sub>n</sub> where n is from 1 to about 6 or 8) groups interposed between the polymer backbone and the pendant phenyl groups, such as resins that have phenyl units of the following Formula IA:



IA

where W\* is a chemical bond or an ester linkage (i.e. (C=O)O); each R', m and Z are the same as defined in Formula I above.

As also discussed, particularly preferred resins of ARCs of the invention have acrylate units in addition to repeat units that have phenyl chromophore units. For example, preferred resins include acrylate copolymers that comprise units represented by the following Formula II:



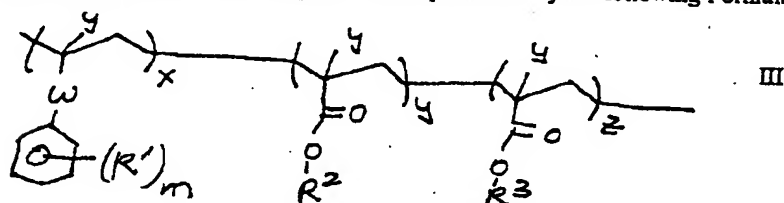
II

wherein W, each R' and m are the same as defined above in Formula I; R<sup>2</sup> is optionally substituted alkyl, preferably having 1 to about 20 carbon atoms, more preferably 1 to about 8 to 12 carbon atoms; optionally substituted carbocyclic aryl such as phenyl; or optionally substituted aralkyl such as optionally substituted benzyl, 2-phenylethyl and the like, and preferably R<sup>2</sup> is a non-aromatic group;

each Y is independently hydrogen or optionally substituted C<sub>1-4</sub> alkyl, and preferably each Y is independently hydrogen or methyl; and

x and y are mole percents of the respective units in the polymer, and preferably x is from about 5 percent to about 80 or 90 percent, more preferably is from about 10 or 15 percent to about 60 or 70 percent, and still more preferably x is from about 20 to about 50 percent, with the balance of the polymer being comprised of units containing R<sup>1</sup> groups, or other units.

Terpolymers and other higher copolymers are especially preferred, such as acrylate copolymers that comprise units represented by the following Formula III:



wherein W, each R' and m are the same as defined above in Formula I;

wherein R<sup>2</sup> and R<sup>3</sup> are each different and are independently selected from the same group as defined above for R<sup>1</sup> in Formula II,

each Y is independently hydrogen or optionally substituted C<sub>1-4</sub> alkyl, and preferably each Y is independently hydrogen or methyl; and

x, y and z are mole percents of the respective units in the polymer, and preferably x is from about 5 percent to about 80 or 90 percent, more preferably is from about 10 or 15 percent to about 60 or 70 percent, and still more preferably x is from about 20 to about 50 percent, with the balance of the polymer being comprised of units containing R<sup>2</sup> and R<sup>3</sup> groups, or other units.

Preferred R<sup>2</sup> and R<sup>3</sup> of the above formulae include hydroxy-substituted alkyl groups, particularly C<sub>1-4</sub> hydroxyalkyl such as 2-hydroxyethyl and hydroxypropyl; alicyclic C<sub>1-4</sub> alkyl such as provided by condensation of methyl methacrylate, methyl

acrylate, ethyl methacrylate, ethyl acrylate, hexyl methacrylate, hexyl acrylate; and cyclic alkyl groups suitably having from 3 to about 20 carbons such as cyclohexyl, adamantyl, isobornyl and the like that may be provided by condensation of the corresponding acrylates and methacrylates.

As indicated above, ARC resins also may have other units such as pendant cyano and itaconic anhydride groups. Preferably, the itaconic anhydride moiety will be directly pendant to the polymer backbone, i.e. the moiety is directly pendant to a polymer bridge group without any alkylene, aryl or other group interposed between the polymer bridge group and the itaconic anhydride group. While the cyano group is preferably directly pendant to the polymer backbone (via condensation of acrylonitrile or the like), a linker group also may be interposed between the cyano group and a polymer bridge group.

As discussed herein, various moieties of an ARC resin or other ARC or resist components may be optionally substituted. A "substituted" substituent may be substituted at one or more available positions, typically 1, 2, or 3 positions by one or more suitable groups such as e.g. halogen (particularly F, Cl or Br); cyano;  $C_{1-8}$  alkyl;  $C_{1-8}$  alkoxy;  $C_{2-8}$  alkenyl;  $C_{1-8}$  alkynyl; hydroxyl; alkanoyl such as a  $C_{1-8}$  alkanoyl e.g. acyl and the like; etc.

Particularly preferred polymers for use in ARCs of the invention include terpolymers of Formula III above where the mole percent on phenyl units (i.e. the value x in Formula III) is from 10 to about 60 percent, more preferably from about 10 or 15 percent to about 40 or 50 percent;  $R^2$  is optionally substituted alkyl particularly  $C_{1-8}$  hydroxyalkyl such as 2-hydroxyethyl, and the mole percent of ester units having  $R^2$  groups (i.e. the value y in Formula III) is from about 1 to 50 or 60 mole percent, more preferably about 10 to 40 or 50 mole percent; and  $R^3$  is unsubstituted alkyl such as  $C_{1-8}$  alicyclic alkyl, e.g. methyl, ethyl, etc., or a cyclic alkyl group and, and the mole percent of ester units having  $R^3$  groups (i.e. the value z in Formula III) is from about 10



to 60 or 70 mole percent, more preferably about 20 or 30 percent to 40 or 50 mole percent; and each Y is independently hydrogen or methyl. See the examples which follow for specifically preferred ARC resins.

ARC resin binders of the invention are preferably synthesized by polymerizing monomers that are the same, or preferably where the monomers differ to provide a copolymer. At least one type of polymerized monomer contains a phenyl group. A free radical polymerization is suitably employed, e.g., by reaction of monomers to provide the various units in the presence of a radical initiator preferably under an inert atmosphere (e.g., N<sub>2</sub> or argon) and at elevated temperatures such as about 70°C or greater, although reaction temperatures may vary depending on the reactivity of the particular reagents employed and the boiling point of the reaction solvent (if a solvent is employed). See the examples which follow for exemplary reaction conditions. Suitable reaction temperatures for any particular system can be readily determined empirically by those skilled in the art based on the present disclosure. A reaction solvent may be employed if desired. Suitable solvents include alcohols such as tetrahydrofuran, propanols and butanols and aromatic solvents such as benzene, chlorobenzene, toluene and xylene. Dimethylsulfoxide and dimethylformamide also can be suitable. The polymerization reaction also may be run neat. A variety of free radical initiators may be employed to prepare the copolymers of the invention. For example, azo compounds may be employed such as Vazo 52 (DuPont), azo-bis-2,2'-isobutyronitrile (AIBN) and 1,1'-azobis (cyclohexanecarbonitrile). Peroxides, peresters, peracids and persulfates also can be employed.

Preferably the ARC resin binder will have a weight average molecular weight (Mw) of about 1,000 to about 10,000,000 daltons, more typically about 5,000 to about 1,000,000 daltons, and a molecular number molecular weight (Mn) of about 500 to about 1,000,000 daltons. Molecular weights (either Mw or Mn) of the polymers of the invention are suitably determined by gel permeation chromatography.

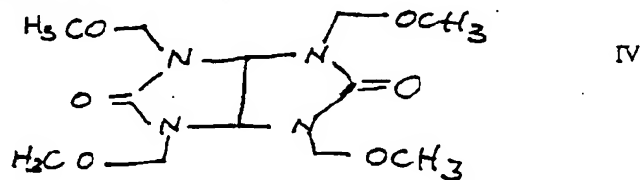
Resin binders of the invention preferably exhibit good absorbance at short wavelengths such as below 200 nm, particularly 193 nm. More specifically, preferred resin binders of the invention have optical densities of at least about 3 absorbance units per micron (Absorb. units/ $\mu$ ) at about 193 nm, preferably from about 5 to 20 or more absorbance units per micron at 193 nm, more preferably from about 8 to 16 or more absorbance units per micron at 193 nm. Higher absorbance values for a particular resin can be obtained by increasing the percentage of chromophore units on the resin.

The antireflective compositions of the invention also may contain resins that do not include phenyl chromophore units as a co-resin present with resins having phenyl chromophore units.

The concentration of the resin binder component of the antireflective compositions of the invention may vary within relatively broad ranges, and in general the resin binder is employed in a concentration of from about 50 to 95 weight percent of the total of the dry components of the ARC, more typically from about 60 to 90 weight percent of the total dry components (all components except solvent carrier).

Crosslinking-type ARCs of the invention also contain a crosslinker component or material. A variety of crosslinkers may be employed, including those ARC crosslinkers disclosed in the above-mentioned Shipley European Application 542008.

Low basicity crosslinkers are particularly preferred such as a methoxy methylated glycouril. A specifically preferred crosslinker is a methoxy methylated glycouril corresponding to the following structure IV:



This methoxy methylated glycouril can be prepared by known procedures. The compound is also commercially available under the tradename of Powderlink 1174 from the American Cyanamid Co.

Other suitable low basicity crosslinkers include hydroxy compounds, particularly polyfunctional compounds such as phenyl or other aromatics having one or more hydroxy or hydroxy alkyl substituents such as a C<sub>1-8</sub> hydroxyalkyl substituents. Phenol compounds are generally preferred such as di-methanolphenol (C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>OH)<sub>2</sub>OH) and other compounds having adjacent (within 1-2 ring atoms) hydroxy and hydroxyalkyl substitution, particularly phenyl or other aromatic compounds having one or more methanol or other hydroxylalkyl ring substituent and at least one hydroxy adjacent such hydroxyalkyl substituent.

Crosslinking antireflective compositions of the invention preferably further comprise an acid or acid generator compound for catalyzing or promoting reaction of the glycouril compound during curing of an ARC coating layer. Preferably an acid generator compound is employed that liberates acid upon photolysis or thermal treatment. Preferably the acid generator is a thermal acid generator is employed, i.e. a compound that generates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, nitrobenzyl tosylate particularly 4-nitrobenzyl tosylate, and other alkyl esters of organic sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Typically a thermal acid generator is present in an antireflective composition in concentration of from about 0.5 to 15 percent by weight of the total of the dry components of the composition, more preferably about 2 percent by weight of the total dry components. Instead of or in addition to a thermal acid generator, a photoacid generator may be employed as an acid generator, and the ARC coating layer blanket exposed to activating radiation prior to application of an overcoated photoresist composition.

Also, rather than an acid generator, an acid may be simply formulated into a crosslinking ARC of the invention, particularly for ARCs that require heating to cure in the presence of acid so that the acid does not promote undesired reaction of composition components prior to use of the ARC. Suitable acids include e.g. strong acids such as sulfonic acids such as toluene sulfonic acid and sulfonic acid, triflic acid, or mixtures of those materials.

The present invention also includes antireflective compositions that do not undergo significant cross-linking during intended use with a photoresist composition. Such non-crosslinking antireflective compositions need not include a crosslinker component or an acid or thermal acid generator for inducing or promoting a crosslinking reaction. In other words, such non-crosslinking antireflective compositions typically will be essentially free (i.e. less than about 1 or 2 weight percent) or completely free of a crosslinker component and/or acid source for promoting a crosslinking reaction.

Antireflective compositions of the invention preferably also comprise one or more photoacid generators (i.e. "PAG") that are suitably employed in an amount sufficient to inhibit or substantially prevent undesired notching or footing of an overcoated photoresist layer. In this aspect of the invention, the photoacid generator is not used as an acid source for promoting a crosslinking reaction, and thus preferably the photoacid generator is not substantially activated during crosslinking of the antireflective composition (in the case of a crosslinking ARC). In particular, with respect to antireflective compositions that are thermally crosslinked, the antireflective composition PAG should be substantially stable to the conditions of the crosslinking reaction so that the PAG can be activated and generate acid during subsequent exposure of an overcoated resist layer. Specifically, preferred PAGs do not substantially decompose or otherwise degrade upon exposure of temperatures of from about 140 or 150 to 190°C for 5 to 30 or more minutes.

Generally preferred photoacid generators for such use in ARCs of the invention include e.g. onium salts such as di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate, halogenated non-ionic photoacid generators such as 1,1-bis[p-chlorophenyl]-2,2,2-trichloroethane, and other photoacid generators disclosed herein for use in photoresist compositions. For at least some antireflective compositions of the invention, antireflective composition photoacid generators will be preferred that can act as surfactants and congregate near the upper portion of the antireflective composition layer proximate to the antireflective composition/resist coating layers interface. Thus, for example, such preferred PAGs may include extended aliphatic groups, e.g. substituted or unsubstituted alkyl or alicyclic groups having 4 or more carbons, preferably 6 to 15 or more carbons, or fluorinated groups such as C<sub>1-15</sub>alkyl or C<sub>2-15</sub>alkenyl having one or preferably two or more fluoro substituents.

Particularly preferred antireflective composition photoacid generators of the invention can be activated upon exposure to sub-200 nm radiation, particularly about 193 nm, so that the antireflective composition can be effectively used with overcoated photoresists that are imaged at 193 nm. Suitably the photoacid generator of the antireflective composition and the photoacid generator of the photoresist composition will be activated at the same exposure wavelength. Sensitizer materials formulated into the photoresist composition and/or antireflective compositions also can be used to ensure that a single exposure wavelength will activate the photoacid generators of both the antireflective and photoresist compositions.

It is further preferred that an antireflective composition of the invention is used together with a photoresist composition where the antireflective composition photoactive compound and photoresist photoactive compound generate the same or approximately the same acid compound (photoproduct) upon exposure to activating radiation during irradiation of the photoresist layer, i.e. photoproducts that preferably have similar diffusion characteristics and similar acid strengths. It has been found that resolution of an overcoated resist relief image is even further enhanced with such

matching of the respective antireflective composition and resist photoacid products. References herein to "substantially the same" antireflective composition and resist photoacid products means that those two photoproducts differ no more than no about 2 or 2.5 in  $pK_a$  values (measured at 25°C), preferably the two photoproducts differ no more than about 1 or 1.5 in  $pK_a$  values, and still further preferably the two photoproducts differ no more than about 0.75 in  $pK_a$  values. It is further preferred that such "substantially the same" antireflective composition and resist photoacid products differ in molecular weight by no more than about 40 percent, preferably by no more than about 20 percent, still more preferably by no more than about 15 percent. It is still further preferred that the antireflective composition and resist photoproducts are each of the same class of acids, e.g. that both photo products are sulfonate acids or both are halo-acids such as HBr and the like. Suitable amounts of the PAG can vary rather widely and can be readily determined empirically. In general, the one or more PAGs of an antireflective composition of the invention may be suitably employed in amounts of about 0.25 to 5 weight percent or less based on total weight of the antireflective composition. See the examples which follow for exemplary amounts. Particularly preferred amounts of a PAG of an antireflective composition also may vary depending on the characteristics and processing conditions of the photoresist that is used with the antireflective composition. For instance, if the photoresist photoacid generator produces a relatively strong acid photoproduct whereby the photoresist is post-exposure baked (PEB) at relatively low temperatures, then the photoacid product of the antireflective composition will be less likely to thermally decompose at such low PEB temperatures, resulting in a relatively higher effective concentration of acid in the antireflective composition. Accordingly, that antireflective composition can be effectively formulated with a relatively lower concentration of photoacid generator. Conversely, if a photoresist is used that is post-exposure baked at relatively high temperatures, then a portion of the photoacid product of the antireflective composition may be more likely to be thermally decomposed. In such case, the antireflective composition may be formulated with a relatively higher concentration of photoacid generator to ensure an effective concentration of photogenerated acid and maximum

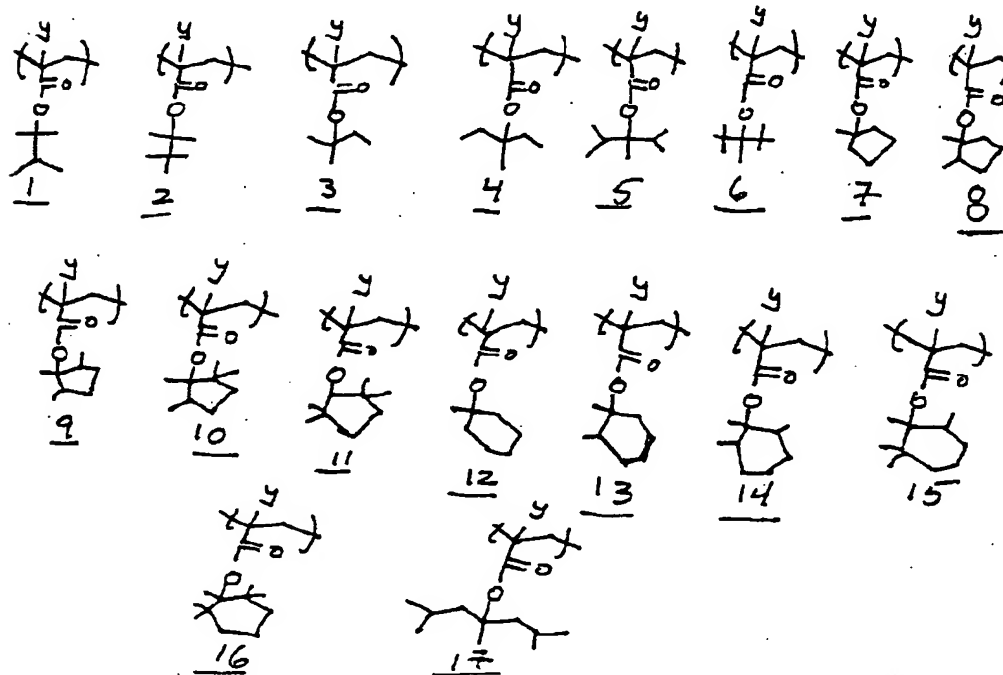
reductions of undesired footing.

Antireflective compositions of the invention also may contain additional dye compounds that absorb radiation used to expose an overcoated photoresist layer. Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604 from Union Carbide, or the surfactant FC 430 available from the 3M Company. Such of such surfactants /surface leveling agents is preferred. Preferred surfactant is concentration between 0.5 to 1.5% of solids, more preferably between about 0.7-1.0 % of solids. See Examples 51-55 which follow.

To make a liquid coating composition, the components of the antireflective composition are dissolved in a suitable solvent such as, for example, ethyl lactate or one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol and ethoxy propanol; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solids content of an antireflective composition varies from about 0.5 to 20 weight percent of the total weight of the antireflective composition, preferably the solids content varies from about 2 to 10 weight percent of the total weight of the antireflective composition.

A variety of photoresist compositions can be employed with the antireflective compositions of the invention, including positive-acting and negative-acting photoacid-generating compositions. Preferably, ARCs of the invention are used with chemically amplified positive-acting resist compositions. Photoresists for use with ARCs of the invention in general contain a resin binder and a photoactive component.

Preferred photoresists for use with the ARCs of the invention are designed for imaging at sub-nm 200 nm wavelengths particularly 193 nm. Preferred resist compositions for use with ARCs of the invention have been disclosed in copending and commonly assigned application serial number 09/143,462, filed on August 28, 1998. In particular, preferred resist resin binders for use with the ARCs of the invention have pendant photoacid-labile ester repeat units that contain a non-cyclic or single ring alkyl group having 5 or more carbons and two or more secondary or tertiary carbon radicals, such as pendant esters of the following structures 1 through 17, and wherein the depicted substituent Y is preferably hydrogen or methyl, more preferably methyl.



Polymers for as a resist resin binder component also may have other units such as pendant cyano and itaconic anhydride groups. Preferably, the itaconic anhydride moiety will be directly pendant to the polymer backbone, i.e. the moiety is directly

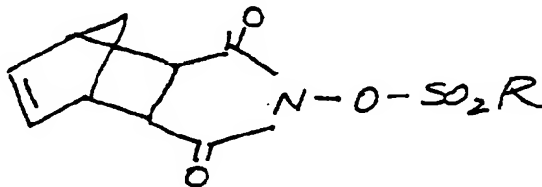


pendant to a polymer bridge group without any alkylene, aryl or other group interposed between the polymer bridge group and the itaconic anhydride group. While the cyano group is preferably directly pendant to the polymer backbone, a linker group also may be interposed between the cyano group and a polymer bridge group.

Polymers used as resin binders of resists of the invention optionally may contain still further units such as groups that contribute to aqueous developability of a photoresist. For example, preferred polymer groups that contribute to aqueous developability contain carboxy or hydroxy moieties such as may be provided by condensation of acrylic acid, methacrylic acid, 2-hydroxyethylmethacrylate, or other monomers. Other optional polymer units include those that may be provided by condensation of a vinyl alicyclic group, e.g. 2-adamantyl-2-methyl methacrylate, isobornyl methacrylate and the like, or a non-cyclic alkyl group such as t-butylmethacrylate and the like. Generally preferred acid labile polymers for use in chemically-amplified photoresists of the invention have one or more polymerized units of monomers of isobornyl methacrylate, methacrylonitrile, itaconic anhydride, methacrylic acid, tert-butyl methacrylate, 2-methyl-2-adamantyl methacrylate or 2,3-dimethyl-2-butyl-methacrylate.

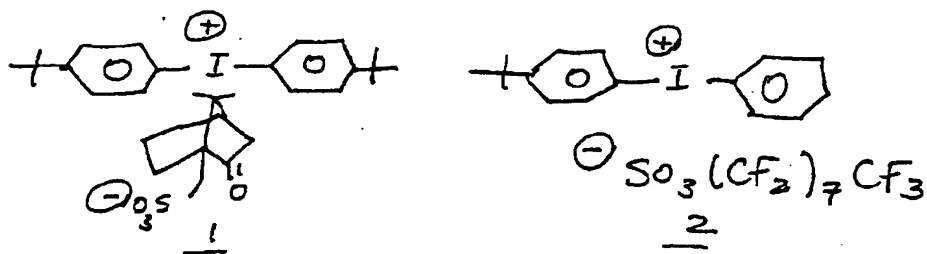
Suitable photoacid generator compounds of resists used with ARCs of the invention include the onium salts, such as those disclosed in U.S. Patent Nos. 4,442,197, 4,603,101, and 4,624,912, each incorporated herein by reference; and non-ionic organic photoactive compounds such as the halogenated photoactive compounds as in U.S. Patent 5,128,232 to Thackeray et al. and sulfonate photoacid generators including sulfonated esters and sulfonyloxy ketones. See *J. of Photopolymer Science and Technology*, 4(3):337-340 (1991), for disclosure of suitable sulfonate PAGs, including benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Preferred sulfonate PAGs are also disclosed in U.S. Patent 5,344,742 to Sinta et al.

Preferred PAGs for photoresists used with ARCs of the invention include imidosulfonates such as compounds of the following formula:



wherein R is camphor, adamantane, alkyl (e.g. C<sub>1-12</sub> alkyl) and perfluoroalkyl such as perfluoro(C<sub>1-12</sub>alkyl), particularly perfluorooctanesulfonate, perfluorononanesulfonate and the like. A specifically preferred PAG is N-[(perfluorooctanesulfonyl)oxy]-5-norbornene-2,3-dicarboximide.

The following PAGs 1 and 2 are also preferred for resists used with ARCs of the invention:



Such sulfonate compounds can be prepared as disclosed in European Patent Application 96118111.2 (publication number 0783136), which details the synthesis of above PAG 1. Briefly, PAG 1 can be prepared by reaction of a mixture of potassium iodate, t-butylbenzene and acetic anhydride with sulfuric acid added dropwise to the mixture with ice-bath cooling. The reaction mixture is then stirred at room temperature for approximately 22 hours, water added with cooling to about 5-10°C and then washing with hexane. The aqueous solution of diaryliodonium hydrogensulfate is then

cooled to about 5-10°C and then camphorsulfonic acid is added followed by neutralization with ammonium hydroxide.

Also suitable are the above two iodonium compounds complexed with anions other than the above-depicted camphorsulfonate and perfluorooctanesulfonate groups. In particular, preferred anions include those of the formula  $\text{RSO}_3^-$  where R is adamantane, alkyl (e.g.  $\text{C}_{1-12}$  alkyl) and other perfluoroalkyl such as perfluoro ( $\text{C}_{1-12}$ alkyl), particularly perfluorobutanesulfonate and the like.

Other known PAGS also may be employed in resists used in accordance with the invention. For 193 nm imaging, generally preferred are PAGS that do not contain aromatic groups, such as the above-mentioned imidosulfonates, in order to provide enhanced resist transparency.

A preferred optional additive of resists of the invention is an added base, particularly tetrabutylammonium hydroxide (TBAH), or tetrabutylammonium lactate, which can enhance resolution of a developed resist relief image. For resists imaged at 193 nm, a preferred added base is a hindered amine such as diazabicyclo undecene or diazabicyclononene. The added base is suitably used in relatively small amounts, e.g. about 0.03 to 5 percent by weight relative to the total solids.

Photoresists of the invention also may contain other optional materials. For example, other optional additives include anti-striation agents, plasticizers, speed enhancers, etc. Such optional additives typically will be present in minor concentrations in a photoresist composition except for fillers and dyes which may be present in relatively large concentrations, e.g., in amounts of from about 5 to 30 percent by weight of the total weight of a resist's dry components.

ARCs of the invention that include a low basicity crosslinker such as a suitable glycouril are particularly useful with photoresists that generate a strong acid

photoproduct upon exposure such as triflic acid, camphor sulfonate or other sulfonic acid, or other acid having a  $pK_a$  (25°C) of about 2 or less. Without wishing to be bound by theory, it is believed ARCs of the invention are particularly effective with such strong acid resists because the strong photogenerated acid will migrate from the resist and remain in the ARC layer to a lesser extent relative to a comparable ARC that contain a more basic crosslinker. That is, the low basicity crosslinkers of the invention will tie up strong photogenerated acids of an overcoated resist layer to a lesser extent than a more basic ARC crosslinker. As a result thereof, less acid loss from the resist layer will occur and resolution problems such as potential footing will be reduced or avoided.

In use, an antireflective composition of the invention is applied as a coating layer to a substrate may any of a variety of methods such as spin coating. The antireflective composition in general is applied on a substrate with a dried layer thickness of between about 0.02 and 0.5  $\mu m$ , preferably a dried layer thickness of between about 0.04 and 0.20  $\mu m$ . The substrate is suitably any substrate conventionally used in processes involving photoresists. For example, the substrate can be silicon, silicon dioxide or aluminum-aluminum oxide microelectronic wafers. Gallium arsenide, ceramic, quartz or copper substrates may also be employed. Substrates used for liquid crystal display or other flat panel display applications are also suitably employed, for example glass substrates, indium tin oxide coated substrates and the like.

Preferably the antireflective layer is cured before a photoresist composition is applied over the ARC. Cure conditions will vary with the components of the ARC. Thus, if the composition does not contain an acid or acid generator, cure temperatures and conditions will be more vigorous than those of a composition containing an acid or acid generator compound. Typical cure conditions are from about 120°C to 225°C for about 0.5 to 40 minutes. Cure conditions preferably render the ARC coating layer substantially insoluble to the photoresist solvent as well as an alkaline aqueous

developer solution.

After such curing a photoresist is applied over the surface of the ARC. As with application of the ARC, the photoresist can be applied by any standard means such as by spinning, dipping, meniscus or roller coating. Following application, the photoresist coating layer is typically dried by heating to remove solvent preferably until the resist layer is tack free. Optimally, essentially no intermixing of the ARC layer and photoresist layer should occur.

The resist layer is then imaged with activating radiation through a mask in conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the resist system to produce a patterned image in the resist coating layer, more specifically, the exposure energy typically ranges from about 3 to 300 mJ/cm<sup>2</sup> depending upon the exposure tool. The exposed resist layer may be subjected to a post-exposure bake if desired to create or enhance solubility differences between exposed and unexposed regions of a coating layer. For example, negative acid-hardening photoresists typically require post-exposure heating to induce the acid-promoted crosslinking reaction, and many chemically amplified positive-acting resists require post-exposure heating to induce an acid-promoted deprotection reaction. Typically post-exposure bake conditions include temperatures of about 50°C or greater, more specifically a temperature in the range of from about 50°C to 160°C.

The exposed resist coating layer is then developed, preferably with an aqueous based developer such as an organic alkali exemplified by tetrabutyl ammonium hydroxide, or an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, sodium metasilicate, aqueous ammonia or the like. Alternatively, organic developers can be used. In general, development is in accordance with art recognized procedures.

The developed substrate may then be selectively processed on those substrates

areas bared of photoresist, for example chemically etching or plating substrate areas bared of photoresist in accordance with procedures well known in the art. Suitable etchants include a hydrofluoric acid etching solution and a plasma gas etch such as an oxygen plasma etch. A plasma gas etch removes the crosslinked antihalation coating layer.

All documents mentioned herein are incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

#### Examples 1-3: Synthesis of Polymers

Example 1: A terpolymer consisting of styrene, 2-hydroxyethylmethacrylate and methylmethacrylate monomers with a mole ratio of 30:38:32 was synthesized according to the following procedure:

The monomers (styrene, 99% pure from Aldrich, 169.79 g; 2-hydroxyethylmethacrylate obtained from Rohm and Haas Corporation "Rocryl 400", 269.10 g; and methylmethacrylate obtained from Rohm & Haas Corporation, 173.97 g), were dissolved in 2375 g of THF in a 5L 3-neck round bottom fitted with overhead stirring, a condenser, and a nitrogen inlet. The reaction solution was degassed with a stream of nitrogen for 20 min. The Vazo 52 initiator (11.63g, from DuPont Corporation) was added and the solution was heated to reflux (65-67°C). This temperature was maintained for 15 hours. The reaction solution was cooled to room temperature and precipitated into 12L of MTBE/cyclohexane (v/v 1/1). The polymer was collected by vacuum filtration and vacuum dried at 50°C for 48 hours. Yield = 68%, and subsequent analysis found the residual monomers = 2.4 wt%, T<sub>g</sub> = 92°C, T<sub>d</sub> = 239°C. The mole concentration of the Vazo 52 initiator relative to the sum of the mole concentration of monomers was 0.72%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a M<sub>w</sub> = 22416, M<sub>n</sub> = 10031.

Examples 2-3: Additional terpolymers of styrene:2-hydroxymethacrylate:methylmethacrylate were synthesized similar to the procedure of Example 1, except that the mole% of the initial monomer amounts were varied according to the following:

Example 2: Polymer with mole% ratio of 12:38:50. Tert-butyl methyl ether (5000 mL) was used as the precipitation solvent. Yield was 168 g (84% of theory). Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 19612$ ,  $M_n = 10434$ , and subsequent analysis found  $T_g = 76^\circ\text{C}$ , and  $T_d = 201^\circ\text{C}$ .

Example 3: A terpolymer consisting of styrene, 2-hydroxyethylmethacrylate and methylmethacrylate monomers with a mole ratio with mole% ratio of 18:38:44. Hexanes (4500 mL) was used as the precipitation solvent. Yield was 68 g (79% of theory). Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 22,712$ ,  $M_n = 11,564$ , and subsequent analysis found  $T_g = 107^\circ\text{C}$ .

Example 4: A terpolymer of styrene:2-hydroxymethacrylate:methylmethacrylate with the monomers in a mole % ratio of 30:38:32 was synthesized according to the procedure of Example 1; with the mole% of the initiator (Vazo 52) at 0.36%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 54502$ ,  $M_n = 22495$ .

Example 5: A tetrapolymer of styrene:2-hydroxymethacrylate:methylmethacrylate:n-butyl methacrylate in a mole % ratio of 30:38:31:1 was synthesized according to the procedure of Example 1; with the mole% of the initiator (Vazo 52) at 0.72%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 22646$ ,  $M_n = 10307$  and subsequent analysis found  $T_g = 74^\circ\text{C}$ ,  $T_d = 331^\circ\text{C}$ .

Example 6: A terpolymer of 4-acetoxystyrene: 2-hydroxymethacrylate: methylmethacrylate was synthesized according to the procedure of Example 1 in a mole % ratio of 18:38:44 Example 1; with the mole% of the initiator (Vazo 52) at 0.36%. Polymer yield was 84%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 73888$ ,  $M_n = 29973$ . Subsequent analysis found  $T_g = 74^\circ\text{C}$ ,  $T_d = 247^\circ\text{C}$ .

Example 7: A terpolymer of phenyl methacrylate: 2-hydroxymethacrylate: methylmethacrylate was synthesized according to the procedure of Example 1 in a mole % ratio of 30:38:32. Example 1; with the mole% of the initiator (Vazo 52) at 0.36%. Yield was 94%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 111039$ ,  $M_n = 26866$ . Subsequent analysis found  $T_g = 91^\circ\text{C}$ ,  $T_d = 242^\circ\text{C}$ .

Example 8: A terpolymer of benzyl methacrylate: 2-hydroxymethacrylate: methylmethacrylate was synthesized according to the procedure of Example 1 in a mole % ratio of 18:38:44 Example 1; with the mole% of the initiator (Vazo 52) at 0.91%. Polymer yield was 99%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 21614$ ,  $M_n = 11379$ .

Example 9: A terpolymer of 2-phenyl-1-ethyl methacrylate: 2-hydroxymethacrylate: methylmethacrylate was synthesized according to the procedure of Example 1 in a mole % ratio of 18:38:44 Example 1; with the mole% of the initiator (Vazo 52) at 0.91%. Polymer yield was 98%. Molecular weight analysis by gel permeation chromatography relative to polystyrene standards gave a  $M_w = 29008$ ,  $M_n = 15956$ .

Example 10: An anti-reflective coating (ARC) composition was prepared using the polymer of Example 1 according to the following procedure: Into a 100 mL bottle



was weighed 1.2175 g of the polymer of Example 1, 0.225 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.0075 g of p-tolyl sulphonic acid, 0.0135g of FC-430 (3M Company), 0.0965 g of di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate (Daychem Corp.) and 48.44 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation), which was placed onto a roller to facilitate dissolution. After dissolution, the ARC composition was filtered through either a 0.1  $\mu\text{m}$  or 0.2  $\mu\text{m}$  Teflon filter into a clean bottle.

Example 11: An anti-reflective coating (ARC) composition was prepared using the polymer of Example 1 according to the following procedure: Into a 100 mL bottle was weighed 1.2175 g of the polymer of Example 1, 0.150 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.075 g of hexamethoxymelamine mixture ("Cymel 303"), 0.0075 g of p-tolyl sulphonic acid, 0.0135g of FC-430 (3M Company), 0.0965 g of di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate (Daychem Corp.) and 48.44 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation), which was placed onto a roller to facilitate dissolution. After dissolution, the ARC composition was filtered through either a 0.1  $\mu\text{m}$  or 0.2  $\mu\text{m}$  Teflon filter into a clean bottle.

Example 12: An anti-reflective coating (ARC) composition was prepared using the polymer of Example 1 according to the following procedure: Into a 500 mL bottle was weighed 4.571 g of the polymer of Example 1, 0.8438 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.0281 g of p-nitrobenzyltosylate, 0.0450g of FC-430 (3M Company), 0.1371 g of di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate (Daychem Corp.) and 48.44 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation), which was placed onto a roller to facilitate dissolution. After dissolution, the ARC composition was filtered through either a 0.1  $\mu\text{m}$  or 0.2  $\mu\text{m}$  Teflon filter into a clean bottle.

Example 13: An anti-reflective coating (ARC) composition was prepared using the polymer of Example 1 according to the following procedure: Into a 100 mL bottle was weighed 1.314 g of the polymer of Example 1, 0.225 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.0075 g of p-tolyl sulphonic acid, 0.0135g of FC-430 (3M Company) and 48.44 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation), which was placed onto a roller to facilitate dissolution. After dissolution, the ARC composition was filtered through either a 0.1  $\mu$ m or 0.2  $\mu$ m Teflon filter into a clean bottle.

Examples 14-18: Anti-reflective compositions were prepared using a procedure and composition very similar to Example 13, with the exception that the amounts of the p-tolyl sulphonic acid and tetramethoxymethyl glycoluril were varied. Table 1 lists the percentages by weight of the total amount of solids in the composition of these two components:

Table 1: ARC compositions

Example	<u>wt% of solids of tetramethoxymethyl glycoluril</u>	<u>wt% of solids of p-tolyl sulphonic acid</u>
14	12	0.1
15	18	0.1
16	15	0.3
17	12	0.5
18	18	0.5

Examples 19-23: Anti-reflective compositions were prepared using a procedure and composition very similar to Example 13, with the exception that the amounts of FC430 was varied. Table 2 lists the percentages by weight of the total amount of solids in the composition of these this component:

Table 2: ARC compositions

<u>Example</u>	<u>wt% of solids of FC430</u>
19	0.2
20	0.5
21	0.8
22	1.1
23	2.0

Examples 24-25: Anti-reflective compositions were prepared using a procedure and composition very similar to Example 13, with the following weights of components in the composition: 0.6102 g of the polymer, 0.1125 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.0030 g of p-tolyl sulphonic acid, 0.0060g of FC-430 (3M Company), 0.0183g of di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate (Daychem Corp.) and 24.25 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation). These compositions are described in Table 3:

Table 3: ARC compositions

<u>Example</u>	<u>Polymer of Example</u>
24	8
25	9

Examples 26-32: Anti-reflective compositions were prepared using a procedure and composition very similar to Example 13, with the following weights of components in the composition: 0.974 g of the polymer, 0.180 g of tetramethoxymethyl glycoluril (American Cyanamid), 0.0060 g of p-tolyl sulphonic acid, 0.0108g of FC-430 (3M Company), 0.0292g of di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate (Daychem Corp.) and 38.80 g of propylene glycol monomethyl ether alcohol ("Dowanol PM", Dow Corporation). ). These compositions are described in Table 4:

Table 4: ARC compositions

<u>Example</u>	<u>Polymer of Example</u>
26	1
27	4
28	6
29	7
30	2
31	3
32	5

**Examples 33-35: Optical Testing of ARC Compositions**

ARC compositions were spin-coated on 200 mm Si wafers and baked at 215°C/90s on a 150  $\mu$ m proximity hotplate using a modern FSI wafer coating track. The ARC films were then measured using a Wollem ellipsometer (Lincoln, NE) to determine their optical indices of refraction n and k (real and imaginary) at 193 nm. The imaginary index of refraction is related to film absorbance; values of about k = 0.3 or greater are necessary to minimize film stack reflectivity while minimizing ARC film thickness. Most desirable are values of about k = 0.4 or greater. These values are tabulated in Table 5:

Table 5: ARC optical parameters measured at 193 nm

<u>Example</u>	<u>real refractive index, n</u>	<u>imaginary refractive index, k</u>
Shipley AR2 (Shipley Corp.)	1.70	0.10
33	1.73	0.216
34	1.74	0.295
35	1.77	0.40

These data illustrate that the comparative material, namely a widely-used commercial ARC material designed for use at 248 nm, Shipley AR2, has an imaginary refractive index significantly lower than what is desired to minimize reflectivity at 193nm. These

data also show that the k-value of compositions 30-32 increase with increasing phenyl moiety in the polymer ( in this case introduced through the styrene monomer). It is the belief of the authors that the phenyl group is a good chromophore at 193 nm , and selecting the ideal phenyl group concentration in the polymer one can achieve a desirable imaginary refractive index, k.

#### Examples 36-40: Evaluation of ARC insolubility after baking

It is strongly desirable that the ARC film is hardened during the coating and baking process such that it becomes impervious to the subsequent coating of photoresist in latter lithographic processing steps. In this invention, ARC hardening during the bake is achieved through chemical acid-catalyzed cross-linking of the polymer. Modern defect-free lithographic processing, particularly for use in semiconductor manufacturing requires that the interface between the resist pattern and the ARC substrate to be as free as possible of scumming, residues and flaring while maintaining an excellent edge acuity. Resist patterns must also adhere well to the ARC during lithographic process steps. In order to meet these requirements, it is the belief of the inventors that intermixing of the resist with the hardened ARC film should be minimized to whatever extent possible.

Several ARC hardened films were studied to determine if they were impervious to dissolution or swelling in a typical commercially-used resist coating solvent, ethyl lactate. Accordingly, the ARC composition was coated on Si, baked at 215°C/60s to yield a 60 nm thick film. The film thickness was then measured at 11 points using a Nanometrics 215 AFT film thickness measuring tool. Then the ARC-coated wafer was immersed in a beaker of ethyl lactate solvent for 60 s. The ethyl lactate was rinsed off with water, and the wafer was air-dried. Film thickness was remeasured at the same positions using the same measuring tool. The change in thickness was recorded. Results are shown in Table 6:

Table 6: Variation in ARC film thickness following a 60s immersion  
in ethyl lactate solvent

<u>Example</u>	<u>Resist Composition</u>	<u>Change in Thickness (Å) after immersion</u>	<u>Comments</u>
36	14	44 Å loss	discolored film
37	15	34 Å loss	discolored film
38	16	0 Å	good quality
39	17	0 Å	good quality
40	18	0 Å	good quality

Examples 38-40 show that compositions 16, 17 and 18 were impervious to either dissolution or swelling in ethyl lactate solvent. This positive result is an indication that these compositions will form subsequent clean interfaces between the resist pattern and the ARC film during standard lithographic patterning. Examples 36-37 show some dissolution of ARC in the resist solvent, indicating that the lithographic processing will likely not be as successful as Examples 38-40. Compositions 16-18 had higher toluene sulphonic acid concentrations in the initial ARC composition (0.3% - 0.5%) as compared to Examples 14 and 15 which had lower acid concentrations (0.1%). As a result, preferred acid concentration in the ARC composition is greater than 0.1%, and more preferably 0.3% or higher. While not being bound by theory, it is believed that the higher acid concentration leads to a higher crosslinking density in the ARC film during baking, making it more impervious to solvent attack. A toluene sulphonic acid concentration of at least 0.3% was therefore used in further ARC material and composition evaluations.

Examples 41-42: Resist compositions used in evaluating ARC efficacy  
Photoresist compositions suitable for lithographic testing was prepared by

dissolving a combination of 0.524 g of perfluoro-octanesulphonate-norbornene dicarboximide, 0.0449g of di(4-tert-butylphenyl)iodonium perfluorooctanesulphonate (DTBIPFOS) and a binder polymer into a stock solution containing 0.0045 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (Aldrich Corp, USA), 0.0075 g of Silwet 7604 (Dow Corning Co., USA) and 43.5 g of propyleneglycol methyl ether acetate (Dow Corp., USA). To aid in dissolving DTBIPFOS, this material was added to the resist composition as 5% solutions in ethyl lactate. After dissolution, the resist composition was filtered through either a 0.1  $\mu\text{m}$  or 0.2  $\mu\text{m}$  Teflon filter into a clean bottle.

Example 41: A binder polymer with a molar feed ratio of 31:22:10:14:23 of isobornyl methacrylate:tert-butyl methacrylate:methacrylic acid:methacrylonitrile:itaconic anhydride was used in the described resist composition. This polymer was prepared through the following procedure:

Into a 500 mL flask was placed 12.54 g of itaconic anhydride, 15.20 g of tert-butyl methacrylate, 4.58 g of methacrylonitrile, 4.28g of methacrylic acid, 33.57g of isobornyl methacrylate, and 100 mL of anhydrous tetrahydrofuran. All reagents were at least 99% pure. The flask was fitted with a magnetic stirring bar, a condenser and an addition funnel. All ingredients were sparged with  $\text{N}_2$  gas for 20 minutes prior to reaction. In the condenser was placed 0.75 g of Vazo52 free-radical initiator and 25 mL of anhydrous tetrahydrofuran. The solution was brought to 70°C, and then the initiator was added over a 20 minute period. The flask was maintained at 70°C for 14 hours, and then cooled to room temperature. Polymer was obtained by precipitation into 3L of hexane, and dried in a Buchner funnel. Then the polymer was re-dissolved into 120 mL of acetone and reprecipitated into 3 L of hexane, and collected on a Buchner funnel. The polymer was dried overnight in a vacuum oven at room temperature. Yield was 49.96g (66%).

Example 42: A binder polymer with a molar feed ratio of 15:10:28:10:14:23 of isobornyl methacrylate:2,3-dimethyl-2-butylmethacrylate:methacrylate:methacrylic acid:methacrylonitrile:itaconic was used in the described resist composition. This

polymer was prepared through a similar procedure as Example 41.

The 2,3-dimethyl-2-butylmethacrylate was synthesized through the following procedure:

Into a 500 mL flask containing a stir bar, and fitted with a condenser, is placed 180g of anhydrous tetrahydrofuran, 40g of 2,3-dimethyl-1-butanol and 40.93 g of triethylamine under a  $N_2$  atmosphere. To this was dropwise added 40.927 g of purified methacryloyl chloride from an addition funnel. The reaction was allowed to warm moderately. After 24 hrs of stirring, the tetrahydrofuran was roto-evaporated from the solution and 100 mL of ethyl acetate was added. The salts were then filtered off through a Buchner funnel. The ethyl acetate was then stripped by use of a rotary-evaporator. A vacuum distillation column was set up with a 8 inch Vigreux column, stir bar and a few small boiling chips. A fractional distillation was performed and 19.8g of the product was recovered in the fraction which had a boiling point of approximately 80 – 87°C at 6-7 torr of pressure.  $^1H$  NMR was used to confirm structure and purity.

#### Example 43 - 64: Lithographic patterning of resist on ARC compositions

In order to assess resolution capability, high-voltage cross-sectional scanning electron microscopic methods were used to examine the printed features. Minimal resolution in an imaged 1:1 pitch grating by choosing an exposure dose such that the patterned 1:1 160 nm lines and 160 nm spaces on the mask actually measured essentially 160nm in size respectively, and then determining the smallest, essentially full-thickness line which cleanly developed, had a flat top and did not leave residue on the substrate. Photospeed is the exposure dose required in forming such a pattern. We found that the photospeed did not vary significantly with the different ARC compositions; The resist composition of Example 41 gave a photospeed of about 29 mJ/cm<sup>2</sup>, and the resist composition of Example 42 gave a photospeed of about 24 mJ/cm<sup>2</sup>.

The lithographic processing was performed on modern wafer-processing tools (manufactured by FSI and SVG Companies) using both 150mm and 200mm silicon



wafers. All processing was done in an essentially base-contaminant free atmosphere (<5 ppb measure amines/ammonia) The wafers were coated with the ARC composition prior to subsequent processing. ARC films were spin-coated and baked at 215°C, with a suitable spin speed chose to yield a thickness of about 65 nm. The photoresist was spun onto the wafers at about 3000 rpm and baked (PAB, post-apply bake) on a 150 µm proximity-gap plate and then rapidly cooled to room temperature to give a film thickness of 4200Å. Then the film was exposed using a resolution-test pattern on a GCA 0.60 NA ArF (193nm) wafer stepper at a partial coherence setting of 0.70. Immediately afterwards, the film was baked (PEB, post-exposure bake) on a 150 µm proximity-gap plate, and then rapidly cooled to room temperature. Immediately afterwards the film was developed using an industry-standard 60 second track-single-puddle process with industry standard 0.26 N tetramethylammonium hydroxide developer.

**Table Z:** Results from lithographic testing of the resist compositions on ARC  
 ResL refers to the resolution at Es. PAB and PEB are given in units of °C and ResL is in units of nm. DUV-18J is a commercial ARC product available from Brewer Sciences Incorporated of Missouri, and AR2 is a commercial ARC product available from Shipley Company of Massachusetts.

<u>Example</u>	<u>ARC of Example</u>	<u>Resist of Example</u>	<u>PAB</u>	<u>PEB</u>	<u>ResL</u>	<u>Resist Profile</u> <u>Comments</u>
44 – comp	DUV 18J	41	140	155	>160	bad summing; flaring
45 – comp	AR2	41	140	155	N/A	resist adhesion failure
46	10	41	140	155	150	good edge acuity
47	11	41	140	155	150	good edge acuity
48	12	41	140	155	150	good edge acuity
49	13	42	140	150	140	good edge acuity
50	16	41	140	155	150	slight scumming
51	19	41	140	155	150	slight scumming
52	20	41	140	155	150	very slight scumming
53	21	41	140	155	150	good edge acuity

Table 7 -cont'd

54	22	41	140	155	150	very slight "pinch"
55	23	41	140	155	150	slight "pinch"
56 - comp	24	41	140	155	160	flaring and scumming
57 - comp	25	41	140	155	155	flaring and scumming
58	26	41	140	155	150	good edge acuity
59	27	41	140	155	150	good edge acuity
60	28	41	140	155	150	good edge acuity
61	29	41	140	155	150	good edge acuity
62	30	41	140	155	150	good edge acuity
63	31	41	140	155	150	good edge acuity
64	32	41	140	155	150	good edge acuity

## Discussion of Examples 17-32:

The compositions of this invention can yield remarkably high-performance ARCs suitable for semiconductor manufacturing applications. The quality of the interface between the resist pattern and the ARC underlayer is sharper and more free of residues, and the resolution capability of the ARC compositions 46-49, 53 and 58-61 exceed the resolution capability of current ARC materials DUV-18J and AR2. The performance of ARC compositions 46-49, 53 and 58-61 also exceed the performance of comparison Examples 56 and 57. Superior performance in compositions 46-49, 53 and 58-61 also illustrate that best results are obtained when the polymers do not contain alkyl spacer group structures between the polymer chain and the phenyl chromophores (for example phenethyl methacrylate in Example 56, and benzyl methacrylate in Example 57).

## Example 65. Testing of reflection control

A primary purpose of the use of an ARC in a lithographic process is to minimize the resist "swing curve"; i.e. minimize the variation in observed photospeed as the resist film thickness is changed. In order to evaluate reflection control, the resist of Example 49 was lithographically processed on the ARC of Example 13 by a process similar to

that of Examples 44-64, except that the ARC film thickness was maintained at 82.5 nm and the thickness of the resist film was varied from 400 nm to 500 nm by changing the resist spin-coating speed. Photospeed to clear (Eo) was measured, and the data are shown below in Table 8:

Table 8: Observed resist photospeed, Eo vs resist film thickness  
on ARC of Example 13

<u>Resist film thickness (nm)</u>	<u>Photospeed to clear, Eo (mJ/cm<sup>2</sup>)</u>
402	7.8
412	7.7
423	7.5
429	7.5
463	8.0
471	7.9
492	7.8

The maximum amplitude in the variation of observed Eo is  $8.0 - 7.5 = 0.5$  mJ/cm<sup>2</sup>. This is a very small variation in photospeed to clear and is acceptable for most modern lithographic processes. This small value illustrates that the compositions of this invention are effective in control of reflection of light from the substrate during exposure at 193nm.

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

1. Abstract

The invention provides new light absorbing crosslinking compositions suitable for use as an antireflective composition (ARC), particularly suitable for short wavelength imaging applications such as 193 nm. The ARCs of the invention are preferably used with an overcoated resist layer (i.e. bottom layer ARCs) and in general comprise novel ARC resin binders that can effectively absorb reflected sub-200 nm exposure radiation.

2. Representative Drawing

Nothing

## \* NOTICES \*

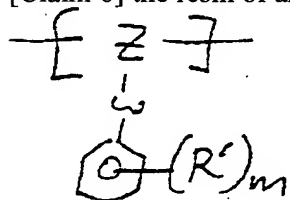
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## CLAIMS

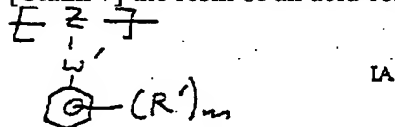
[Claim(s)]

- [Claim 1] (a) Prepare on a substrate the layer of the acid-resisting constituent containing the resin binder which has a phenyl group;  
 (b) Harden an acid-resisting constituent layer;  
 (c) Prepare the layer of a photoresist constituent on the layer of an acid-resisting constituent;  
 (d) The approach containing developing-layer of photoresist which exposed photoresist layer with activation exposure light, and was exposed; for forming a photoresist relief image.
- [Claim 2] The approach according to claim 1 of exposing a photoresist layer with the activation exposure light which has the wavelength of less than about 200nm.
- [Claim 3] The approach according to claim 1 of exposing a photoresist layer with the activation exposure light which has the wavelength of about 193nm.
- [Claim 4] The approach according to claim 1 in which the phenyl group is carrying out direct suspension to the principal chain of the resin of an acid-resisting constituent.
- [Claim 5] The approach according to claim 1 the phenyl group is carrying out suspension to the principal chain of the resin of an acid-resisting constituent, and any alkyl units do not intervene between the principal chain of resin, and a phenyl group.
- [Claim 6] the resin of an acid-resisting constituent -- degree type I: -- [Formula 1]



(-- the inside of a formula, and W -- chemical bond, alkyl association, or ester bond; -- hydrogen, a permutation or unsubstituted alkyl, a permutation or unsubstituted alkoxy \*\* ester, a permutation or unsubstituted alkanoyl, a permutation, unsubstituted ring type aryl, a permutation, or unsubstituted aralkyl; m of R' each is a joint radical independent [ each Z / integers / from 0 to 5 /; and / between polymer units ].) -- approach including a unit according to claim 1.

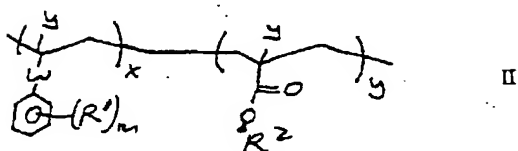
[Claim 7] the resin of an acid-resisting constituent -- degree type IA: -- [Formula 2]



(-- inside of formula, and W' -- chemical bond or ester bond; -- as for R' each, as for hydrogen, a permutation or unsubstituted alkyl, a permutation or unsubstituted alkoxy \*\* ester, a permutation or unsubstituted alkanoyl, a permutation, unsubstituted ring type aryl, a permutation, or unsubstituted aralkyl; m, each Z [ integers / from 0 to 5 /; and ] is the joint radical which it became independent of between polymer units.) -- approach including a unit according to claim 1.

[Claim 8] The approach according to claim 1 the resin in an acid-resisting constituent is acrylate resin.

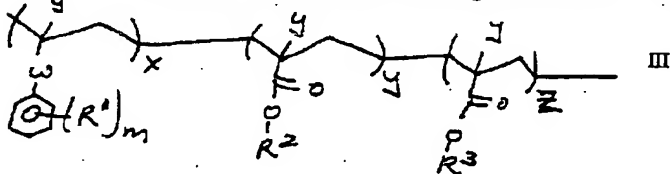
[Claim 9] the resin of an acid-resisting constituent -- degree type II: -- [Formula 3]



the inside of a formula, and W -- chemical bond, alkyl association, or ester bond; -- every -- R1 Hydrogen, a permutation or unsubstituted alkyl, a permutation, or unsubstituted alkoxy \*\* Ester, a permutation or unsubstituted alkanoyl, a permutation, unsubstituted ring type aryl, a permutation, or an unsubstituted aralkyl; R2 A permutation, unsubstituted alkyl, a permutation, or unsubstituted ring type aryl; hydrogen [ with Y / independent each ], permutation, or one to C6 unsubstituted alkyl; x, and y are an approach including the unit of mol %; of each unit in resin according to claim 1.

[Claim 10] The approach according to claim 9 R2 contains a hydroxyl group in the above-mentioned general formula II.

[Claim 11] the resin of an acid-resisting constituent -- degree type III: -- [Formula 4]



the inside of a formula, and W -- chemical bond, alkyl association, or ester bond; -- R'each Hydrogen, a permutation or unsubstituted alkyl, a permutation, or unsubstituted alkoxy \*\* Ester, a permutation or unsubstituted alkanoyl, a permutation, unsubstituted ring type aryl, a permutation, or an unsubstituted aralkyl; R2 and R3 different, respectively permutation [ independent ], unsubstituted alkyl, permutation, or unsubstituted ring type aryl; -- hydrogen with Y [ independent each ], a permutation, or one to C6 unsubstituted alkyl; And x, and y and z are mol% of each unit in resin. An approach including a unit according to claim 1.

[Claim 12] The approach according to claim 11 at least one of the R2 or R3 substituents has a hydroxyl group in the above-mentioned general formula III.

[Claim 13] The approach according to claim 1 an acid-resisting constituent contains a heat acid generator compound.

[Claim 14] The approach according to claim 1 of hardening an acid-resisting constituent thermally, before preparing a photoresist constituent layer.

[Claim 15] The approach according to claim 1 by which an acid-resisting constituent is not substantially activated until the photo-oxide generating agent exposes a photoresist constituent layer including a photo-oxide generating agent.

[Claim 16] The approach according to claim 1 an acid-resisting constituent contains the cross linking agent matter.

[Claim 17] The approach according to claim 1 a photoresist constituent is the positive type amplified chemically.

[Claim 18] (a) Prepare on a substrate the layer of the acid-resisting constituent containing the resin binder which has a phenyl group.;

(b) Prepare the layer of a photoresist constituent on the layer of an acid-resisting constituent.;

(c) The approach containing developing-layer of photoresist which exposed photoresist layer with activation exposure light, and was exposed; for forming a photoresist relief image.

[Claim 19] The approach according to claim 18 of exposing a photoresist layer with the activation exposure light which has the wavelength of less than about 200nm.

[Claim 20] The approach according to claim 18 in which the phenyl group is carrying out direct suspension to the principal chain of the resin of an acid-resisting constituent.

[Claim 21] (1) Spreading layer of the acid-resisting constituent containing the resin which has a phenyl group;

(2) The applied substrate containing the applied substrate which has spreading layer; of a photoresist layer on it on an acid-resisting constituent layer.

[Claim 22] The acid-resisting constituent of the bottom layer containing the resin which has a phenyl group

used in order to carry out image formation of the finished photoresist in the wavelength of less than 200nm.

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**DETAILED DESCRIPTION**


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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the constituent which decrease in number reflection by back track of the exposure exposure light to the photoresist layer finished from the substrate. This invention relates to a detail more at the acid-resisting covering constituents (ARCs) containing the resin binder which absorbs effectively the short wavelength exposure exposure light containing less than 200nm exposure light like 193nm exposure light.

[0002]

[Description of the Prior Art] A photoresist is a film used in order to imprint an image to a substrate. The spreading layer of a photoresist is formed on a substrate and, subsequently a photoresist layer is exposed through a photo mask by the source of an activation exposure. A photo mask has an opaque field and the field of an and also [ it is transparence to activation exposure light ] to activation exposure light. If activation exposure light is exposed, a photoresist coat will produce the chemical denaturation (photo induced chemical transformation) by which induction was carried out to light, and the substrate to which the pattern of a photo mask applied the photoresist by it will imprint. Development of a photoresist obtains after exposure the relief image which can alternative process a substrate.

[0003] The photoresist is possible also at a positive type or a negative mold. In the case of most negative-mold photoresists, the part exposed by the activation exposure light of a spreading layer performs a polymerization or bridge formation in the reaction between the photosensitive compound of a photoresist constituent, and the reagent in which a polymerization is possible. Therefore, it is hard coming to dissolve the exposed spreading part with a development solution rather than the part which is not exposed. The field which becomes easy to dissolve the part which was exposed in the case of the positive type photoresist with a development solution, and is not exposed on the other hand maintains the condition of being hard to dissolve with a developer in comparison. The photoresist constituent is well-known to this contractor. "The photoresist ingredient and approach" (Photoresist Materials and Prosesses)" () by De Forest (Deforest) [ McGraw Hill Book Company, ] [ New ] " York, Chapter 2 of 1975, and Molly (Moreay) Semi-conductor lithography, It actually reaches and is indicated by Chapter 2 of ingredient (Semiconductor Lithography, Principles Practies and Materials)" (Plenum Press, New York), and Chapter 4. a principle -- Also in this invention, it is referring to [ reference / this / both ] about the instruction about a photoresist constituent, and its manufacturing method and usage.

[0004] in a semi-conductor, the main applications of a photoresist come out, and there are, and one purpose is changing into the complicated matrix of the electronic conduction path of a desirable a micron or submicron geometric pattern the flake of the semi-conductor ground by altitude, such as silicon or gallium arsenide, in order to make the function as a circuit discover. It is a key for processing a photoresist appropriately to attain this purpose. Although strong interdependence is among various photoresist processing processes, in obtaining the photoresist image of high resolution, exposure is considered to be one of the more important processes.

[0005] Reflection of the activation exposure light often used in order to expose a photoresist may present the limit of the image by which pattern formation was carried out in the photoresist layer. If exposure light reflects from a substrate / photoresist interface, the exposure reinforcement in the photoresist between exposure may change, and the line breadth of a photoresist will become an ununiformity by it at the time of development. Since exposure light is scattered about to the photoresist field which is not made into the purpose of exposure from a substrate / photoresist interface, line breadth will vary also in this case. Extent of dispersion or reflection changes with fields typically, and line breadth becomes an ununiformity further also



by this. The reflective problem to which the change in the configuration of a substrate also presents a limit to resolution is caused.

[0006] From the latest inclination for the semiconductor device to serve as high density, there is an inclination which shortens wavelength of the source of exposure to far-ultraviolet (DUV) light (wavelength of 300nm or less), KrF excimer laser light (248.4nm), ArF excimer laser light (193nm), an electron beam, and soft X ray in the industrial world. Since the shortened wavelength was used in order to carry out image formation to a photoresist coat, generally the reflection from the upper resist front face increased like the front face of a lower layer substrate as a result. Therefore, using shorter wavelength has enlarged the problem of the reflection from a substrate front face.

[0007] By another technique used in order to lessen the problem of the reflected light, the exposure light absorption layer inserted between a substrate front face and a photoresist enveloping layer has been used. For example, please refer to the PCT application public presentation official report 90th / No. 03598 (W090/03598), the European Patent application public presentation official report No. (1 EP, A 0,639,941) 0639941 and U.S. Pat. No. 4,910,122, 4,370,405, and 4,362,809. Refer for these by this invention about the indication of an acid-resisting (antihalation) constituent and its usage to all. Such a layer is described also in said reference by expression called an acid-resisting layer or ARC (acid-resisting constituent). The very useful antihalation (acid resisting) constituent is indicated by the European Patent application public presentation official report No. (EP, A1,542,008) 542008 of a cypripedium rhe company (Shipley Co.).

[0008]

[Problem(s) to be Solved by the Invention] While it is found out that the ARC constituent in the advanced technology is effective in many acid-resisting applications, especially the constituent of the advanced technology has the constraint on some engine performance, when it is used for a short wavelength image formation application. Therefore, to have a new antireflection coating constituent is desired. A new antireflection coating constituent which contains less than (sub-200nm) 200nm exposure light like 193nm especially and which absorbs effectively the reflection which is not desirable as for the exposure light of short wavelength is desired.

[0009]

[Means for Solving the Problem] This invention offers a suitable new light absorption constituent to use it as an antireflection coating constituent (ARC) to a short wavelength image formation application like especially 193nm image formation. ARC(s) of this invention also contain a cross linking agent component as occasion demands including the resin binder which short wavelength exposure light is absorbed [ binder ] effectively, and generally decreases reflection of this exposure light.

[0010] The desirable resin binder of ARC(s) of this invention includes the phenyl unit which carried out suspension to the polymer principal chain preferably. Especially the desirable ARC resin binder of this invention does not have any alkyl (for example, it is permutation or unsubstituted n (-CH<sub>2</sub>-), and n is 1 to about 6, or 8.) units which intervene between the phenyl units which carried out suspension to the polymer principal chain. For example, the desirable radical which carried out suspension contains what is obtained by the polymerization of a permutation or unsubstituted styrene, a permutation or unsubstituted isopropyl styrene, a permutation or unsubstituted acrylic-acid phenyl and a permutation, or unsubstituted methacrylic-acid phenyl. The phenyl group "carried out direct suspension" (directly pendant) from the polymer principal chain stated by this invention shows that an alkyl group or other radicals do not intervene between a polymer principal chain and a phenyl group so that it may be obtained by the polymerization of a permutation, unsubstituted styrene, a permutation, or an unsubstituted isopropyl styrene unit.

[0011] However, although it is not so desirable, this invention includes ARC(s) which have a resin binder with the phenyl group to which alkyl (for example, it is permutation or unsubstituted n (-CH<sub>2</sub>-), and n is 1 to about 6 or 8.) association intervenes between a polymer principal chain which is obtained by the polymerization of for example, methacrylic-acid-2-phenylethyl and its analogue, and a phenyl group, and which carried out suspension.

[0012] The acid-resisting constituent resin binder with a phenyl chromophore part is a copolymer suitably, it is preferably based on the polymerization of a different monomer beyond 2 or it, and at least one of the monomer of the contains a phenyl chromophore group. For example, another desirable ARC resin unit is for example, methacrylic-acid-2-hydroxyethyl, acrylic-acid-2-hydroxyethyl, and hydroxy acrylate like those analogue.; What is obtained by the polymerization of an acrylate monomer like a methyl methacrylate, a methyl acrylate, methacrylic-acid butyl, butyl acrylate, and one to C12 acrylate like those analogue is included. As for acrylate resin including a phenyl chromophore unit, being used in ARC(s) of this invention generally is desirable. In order to construct a bridge in ARC(s) of this invention, ARC resin has the hydroxyl

group or other reactant parts for promoting a hardening reaction preferably.

[0013] This invention offers the new manufacturing technology containing the new approach of forming a relief image further, and the substrate which is ARC constituent independent [ of this invention ], or was applied in combination with a photoresist constituent. Other modes of this invention are indicated below.

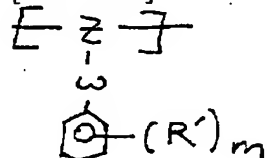
[0014]

[Embodiment of the Invention] As for the resin binder constituent of the acid-resisting constituent of this invention, it is desirable to use it with the image formation system of short wavelength, and reflection of less than 200nm and the reflection which is especially 193nm are absorbed effectively.

[0015] Especially the desirable ARC resin binder of this invention has the phenyl group which carried out suspension. For example, desirable resin has the phenyl unit shown by the degree type I.

[0016]

[Formula 5]

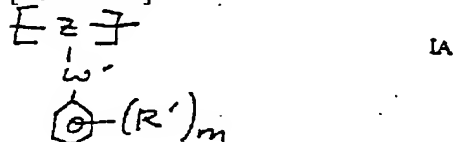


[0017] the inside of a formula, and W -- a chemical bond, alkyl association, for example, a permutation, or unsubstituted n (-CH<sub>2</sub>-) -- it is -- n -- 1 to about 6, 8, or ester bond (namely, O (C=O)); -- R' each alkoxy \*\* non-hydrogen substituent; like hydrogen or a halogen (F, Cl, Br, or I) -- the permutation which has one piece to about eight carbon atoms preferably, or unsubstituted alkyl; -- the permutation which has one piece to about eight carbon atoms preferably, or unsubstituted A permutation like one to C<sub>8</sub> alkanoyl whose Z is the permutation or unsubstituted alkyl; for example, the acyl, and the similar radical of C 1-8 with the permutation or the unsubstituted ester like C(=O) OZ, or unsubstituted alkanoyl; - A permutation or unsubstituted ring type aryl, Especially, phenyl; permutation or unsubstituted aralkyl especially benzyl (-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>);, and similar radical;m Integer; and Z of 0 to 5 (when the phenyl group which carried out suspension is completely permuted from hydrogen) it is a joint radical between the monomeric units of a polymer, for example, of a reaction component of a monomeric unit like a carbon-carbon double bond, a polymerization is carried out, for example, a permutation or unsubstituted alkylene, and one to C<sub>3</sub> alkylene that was permuted by one to C<sub>4</sub> alkyl, or is not carried out are given preferably.

[0018] As mentioned above, although more desirable resin has the phenyl group which carried out suspension, it is resin without any alkyl (for example, it is permutation or unsubstituted n (-CH<sub>2</sub>-), and n is 1 to about 6, or 8.) radicals which intervene between the phenyl groups which carried out suspension to the polymer principal chain, for example, resin with the phenyl unit shown by the degree type IA.

[0019]

[Formula 6]

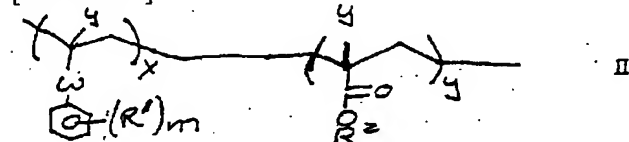


[0020] (inside of formula, and W' -- chemical bond or ester bond (namely, O (C=O)); -- every R', and m and Z are the same as what was defined by the above-mentioned formula I.)

Moreover, in addition to a repeat unit with a phenyl chromophore unit, especially the desirable ARC resin of this invention has an acrylate unit as mentioned above. For example, the acrylate copolymer which consists of the unit expressed with the degree type II as desirable resin is mentioned.

[0021]

[Formula 7]



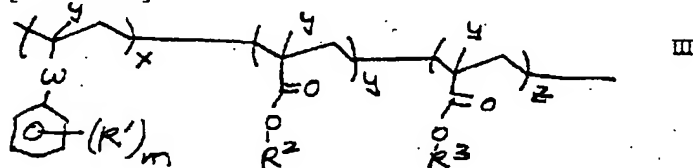
[0022] (The inside of a formula, W, every R', and m are the same as what was defined by the above-

mentioned formula I.;R2) Preferably The carbon atom, the more desirable permutation of the carbon atom of 1 to about 8 thru/or 20 or more desirable unsubstituted permutations, such as alkyl group; phenyl, or unsubstituted ring type aryl of 1 to about 20, Or it is a permutation like a permutation or unsubstituted benzyl, 2-phenylethyl, and a similar radical, or an unsubstituted aralkyl, and R2 is a non-aromatic series radical preferably. the hydrogen or the permutation which Y became independent of each, or one to C6 unsubstituted alkyl -- and preferably Hydrogen or methyl; which Y became independent of each, and x and y It is the mole percent of each unit in a polymer. x preferably About 5% to about 80 thru/or 90%, more preferably, from about 10 thru/or 15%, 70%, it is about 50% from about 20% further more preferably, and the remainder of a polymer includes about 60 thru/or a unit including R2 set or other units.

[0023] Especially an acrylate copolymer including the unit shown by the copolymer and the copolymer [ pluralism / ones / other ] III, for example, a degree type, etc. is desirable. [ of 3 yuan ]

[0024]

[Formula 8]



[0025] (The inside of a formula, W, every R', and m are the same as what was defined by the above-mentioned formula I. R2 and R3 among; type) it differs, respectively and chooses independently of the same radical as what was defined by R2 in Formula II -- having --; -- Y each hydrogen, the independent permutation, or independent unsubstituted C -- preferably one to 6 alkyl Hydrogen or methyl; which Y became independent of each, x, and y and z It is the mole percent of each unit in a polymer. Preferably x does not have about 80 from about 5%, there is no about 60 [ 90% ] from about 10 thru/or 15% more preferably, and x is about 50% from about 20% further more preferably 70%. the remainder of a polymer consists of R2 set, R3 set, or a unit including other units.

[0026] R2 and R3 with the above-mentioned desirable formula A hydroxy-permutation alkyl group, a C1-6 hydroxyalkyl; methyl methacrylate especially like 2-hydroxyethyl and hydroxypropyl, A methyl acrylate, ethyl methacrylate, an ethyl acrylate, methacrylic-acid hexyl, One to alicyclic C8 alkyl which is obtained by the polymerization of acrylic-acid hexyl; It reaches. The annular alkyl group which has three pieces to about 20 carbon, such as cyclohexyl, adamantyl, isobornyl, and a similar radical, suitably, and is obtained by the polymerization of corresponding acrylate and methacrylate is included.

[0027] As described above, ARC resin may have other units, such as a cyano \*\*\*\*\* itaconic-acid-anhydride radical which carried out suspension. Preferably, the direct suspension of the itaconic-acid-anhydride part is carried out to a polymer principal chain, namely, the direct suspension of the part concerned is carried out to a polymer joint radical, without having the alkylene which intervenes between a polymer joint radical and an itaconic-acid-anhydride radical, aryl, or other radicals. On the other hand, although the direct suspension of this cyano group is preferably carried out to this polymer principal chain (acrylonitrile or polymerization of a prototype), a joint radical may intervene between this cyano group and a polymer joint radical.

[0028] As discussed by this invention, as long as ARC resin, other ARC(s), or the various parts of a resist component are requests, they may be permuted. The substituent "permuted" is set on one piece or the replaceable location beyond it, and a general target at 1, 2, or the 3rd place. for example, a halogen (especially -- F --) Cl or Br; cyano; -- one to C8 alkyl; -- C1-8 alkoxy; -- two to C8 alkenyl; -- two to C8 alkynyl; -- it may permute by one piece or the suitable radicals beyond it, such as alkanoyl [ , such as one to C6 alkanoyl, such as hydroxyl; , for example, acyl, and a similar radical, ];

[0029] Especially the desirable polymer used for ARC(s) of this invention The mole percent (namely, value of x in Formula III) of a phenyl unit From 10% to about 60% More preferably about 40 thru/or 50 %;R2 from about 10 thru/or 15% It is one to C6 hydroxyalkyl, such as a permutation or unsubstituted alkyl, especially 2-hydroxyethyl. The mole percent (namely, value of y in Formula III) of an ester unit with R2 set 50 from about 1 mole percent thru/or 60 mole percents, More preferably 40 thru/or 50 mole-percent;R3 from about 10 mole percents For example, they are unsubstituted alkyls, such as C1-8 alicyclic alkyls, such as annular alkyl groups, such as methyl and ethyl. The mole percent (namely, value of z in Formula III) of

an ester unit with R3 set 60 from about 10 mole percents thru/or 70 mole percents, more -- desirable -- 40 thru/or 50 mole percent [ from about 20 thru/or 30 mole percents ]; -- Y contains each the 3 yuan copolymer of the above-mentioned formula III which is independent hydrogen or methyl. Please refer to the below-mentioned example especially about desirable ARC resin.

[0030] The ARC resin binder of this invention is suitably compounded by carrying out the polymerization of the monomer from which it differs the same monomer or for obtaining a copolymer preferably. At least one sort of monomers by which the polymerization was carried out contain a phenyl group. The free radical polymerization by making the monomer which are the elevated temperatures above about 70 degrees C under an inert atmosphere (for example, nitrogen or an argon) preferably, and offers various units, for example under existence of a radical initiator react (when using a solvent), although reaction temperature may change by the boiling point of the reactivity of the specific reagent to be used and a reaction solvent is used suitably. Refer to the below-mentioned example for the example of a reaction condition. By the indication of this invention, this contractor can decide suitable reaction temperature also to all specific systems experientially. A reaction solvent may be used as long as it is a request. As a suitable solvent, an aromatic series solvent like benzene, a chlorobenzene, toluene, and a xylene etc. is mentioned to alcohol like a tetrahydrofuran, propanol, and a butanol, and a list. Dimethyl sulfoxide and dimethylformamide are also suitable. Moreover, a polymerization reaction can also carry forward a non-solvent. The copolymer of this invention may be prepared using various free radical initiators. For example, Vazo An azo compound like 52 (Du Pont), the azo-screw -2, and - isobutyronitrile (azobisisobutyronitrile), and 2 '1, 1'-azobis (cyclohexane carbonitrile) may be used. A peroxide, peroxy-acid ester, a peroxy acid, and persulfate may also be used.

[0031] As for an ARC resin binder, it is desirable to have about 10,000,000dalton of the weight average molecular weight (Mw) of about 5,000 to about 1,000,000dalton and the number average molecular weight (Mn) of about 500 to about 1,000,000dalton more generally from about 1,000. The molecular weight (Mw and Mn) of the polymer of this invention is suitably calculated by the gel permeation chromatography.

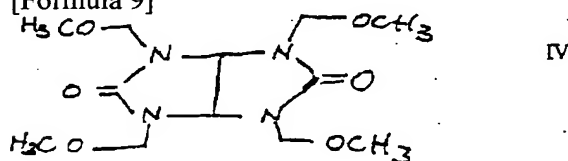
[0032] The resin binder of this invention has less than 200nm and the desirable thing which shows a good absorbance especially with the short wavelength of 193nm. even if there are few resin binders with this invention more desirable in a detail per micron in about 193nm -- the optical density of about 3 absorbances (an absorbance/mu), and 193nm of good better \*\* -- setting -- about 5 to 20, or the absorbance per micron beyond it -- in 193nm of good better \*\*, it has an absorbance per micron beyond about 8 to 16, or it more. The value of the higher absorbance which is the need can be acquired by increasing the percent of the chromophore unit of resin to characteristic resin. Moreover, the acid-resisting constituent of this invention can contain resin without a phenyl chromophore unit as \*\*\*\*\* (co-resin) which coexists with resin with a phenyl chromophore unit.

[0033] The concentration of the resin binder component of the acid-resisting constituent of this invention can be changed in the comparatively large range, and, still more generally a resin binder is usually used 95 percentage by weight from about 50 of all the desiccation components of ARC by the concentration to about 60 to 90 of all desiccation components (all components except a solvent carrier) percentage by weight.

[0034] The bridge formation mold ARC of this invention also contains a cross linking agent component or the matter. Various cross linking agents can be used and the ARC cross linking agents currently indicated by the European Patent application No. 542008 of the aforementioned cypridium rhe company (Shipley Co.) are mentioned into it. As a cross linking agent, especially the cross linking agent of whenever [ like methoxymethyl-ized glycouril (glycouril) / low-salt radical ] is desirable. As a desirable cross linking agent, there is methoxymethyl-ized glycouril corresponding to the following structure expression IV especially.

[0035]

[Formula 9]



[0036] This methoxymethyl-ized glycouril can be prepared in a well-known procedure. Moreover, this compound is marketed by the trade name of the powder link (Powderlink) 1174 from the American cyanamide company (American Cyanamid Co.).

[0037] As a cross linking agent, a hydroxy compound and a multifunctional compound like aromatic series

which has a hydroxyalkyl substituent like a phenyl group, at least one hydroxy group, or a C1-8 hydroxyalkyl substituent especially are mentioned whenever [ other suitable low-salt radical ]. Generally the phenyl group or other aromatic compounds which have other compounds with the substituent of a dimethanol phenol ( $C_6H_3(CH_2OH)_2OH$ ), an adjoining hydroxy group (atom of the location of 1-2 of a ring), and a hydroxyalkyl radical and at least one hydroxy group which adjoins at least one methanol or other hydroxyalkyl ring substituents, and a hydroxyalkyl substituent especially as a phenolic compound are desirable.

[0038] While stiffening an ARC coating layer, in order to cause a catalyst or a promotion operation to the reaction of this glycouril compound, the bridge formation mold acid-resisting constituent of this invention contains an acid or an acid generator compound further preferably. Preferably, the acid generating compound which generates an acid is used at the time of a photolysis or heat treatment. Preferably, a heat acid generator, i.e., the compound which generates an acid at the time of heat treatment, is used as an acid generator. 2, 4, 4, 6-tetrabromo cyclohexa JIENON, benzoin tosylate, nitrobenzyl tosylate, and various well-known heat acid generators especially like the alkyl ester of 4-nitrobenzyl tosylate and other organic sulfonic acids are used suitably. Generally the compound which generates a sulfonic acid is suitable at the time of activation. Typically, a heat acid generator exists in an acid-resisting constituent more preferably by the concentration of about 2 percentage by weight of all desiccation components the 0.5 to 15 percentage by weight abbreviation of all the desiccation components of an acid-resisting constituent. As instead of or an addition of a heat acid generator, a photo-oxide generating agent can use it as an acid generator, and an ARC coating layer blanket is exposed by activation exposure light before spreading of the finished photoresist constituent.

[0039] Moreover, it is used, when it is ARC(s) which need to be heated under existence of an acid to make it harden so that an acid may only be blended into the bridge formation mold ARC of this invention and an acid may not promote rather the reaction which is not desirable as for a constituent component before use of ARC especially instead of an acid generator. As a suitable acid, strong acid like sulfonic acids, such as toluenesulfonic acid, a sulfonic acid, and a triflic acid (triflic acid), or those mixture are mentioned, for example.

[0040] This invention also contains the acid-resisting constituent with which remarkable bridge formation does not take place in process of use with the photoresist constituent made into the purpose. Such an acid-resisting constituent of the mold non-constructing a bridge does not need to include crosslinking reaction for induction, the cross linking agent component for making it promote, an acid, or a heat acid generator. In other words, generally, such an acid-resisting constituent of the mold non-constructing a bridge does not contain essentially (namely, about 1 or under the amount percent of duplexes), or completely the cross linking agent component and/or acid source of supply for promoting crosslinking reaction.

[0041] Moreover, the acid-resisting constituent of this invention contains one or more sorts of photo-oxide generating agents (namely, "PAG") suitably used in the amount which controls enough finished notching (notching) or the footing (footing) of a photoresist layer which is not desirable, or is prevented substantially preferably. In this mode of this invention, a photo-oxide generating agent is not used as an acid source of supply for promoting crosslinking reaction, therefore a photo-oxide generating agent is not preferably activated substantially in process of bridge formation of an acid-resisting constituent (in the case of the bridge formation mold ARC). The acid-resisting constituent PAG should be substantially stable to crosslinking reaction conditions so that it may activate in the next exposure process of the photoresist layer by which this PAG was finished about the acid-resisting constituent over which a bridge is constructed especially thermally and an acid may be generated. When the temperature of about 140 degrees C or 150 degrees C - 190 degrees C is made to expose especially desirable PAG 30 minutes or more than it from 5 minutes, it does not decompose or deteriorate substantially.

[0042] as the desirable photo-oxide generating agent which is generally used for ARC(s) of this invention -- for example, JI (4-t-buthylphenyl) iodonium onium salt [ , such as a perfluoro-octane sulfonate, ], 1, and 1-screw [p-chlorophenyl] - in order to use it with the photo-oxide generating agent and photoresist constituent of a halogenation non-ion system like 2, 2, and 2-trichloroethane, other photo-oxide generating agents currently indicated by this specification are mentioned. The photo-oxide generating agent for acid-resisting constituents which acts as a surface active agent at least to some acid-resisting constituents of this invention, and gather near the upper part of an acid-resisting constituent layer near the interface of an acid-resisting constituent / resist spreading layer is desirable. Long-chain aliphatic series radicals, such as the permutation or the unsubstituted alkyl group which follows, for example, has four or more carbon, and six - 15 carbon, one piece, one to C15 desirable alkyl that has two or more fluorine substituents preferably or a fluorinated

desirable radical like two to C15 alkenyl as such desirable PAG, or an alicyclic radical, are mentioned. [0043] Less than 200nm, especially the desirable photo-oxide generating agent especially for the acid-resisting constituents of this invention is activated, when it exposes with 193nm exposure light, consequently an acid-resisting constituent is effectively used with the finished photoresist by which image formation is carried out with 193nm light. As for the photo-oxide generating agent of an acid-resisting constituent, and the photo-oxide generating agent of a photoresist constituent, activating on the same exposure wavelength is desirable. Moreover, the sensitizer blended with a photoresist constituent and/or an acid-resisting constituent is used in order to activate certainly the photo-oxide generating agent of both acid resisting and a photoresist constituent with single exposure wavelength.

[0044] Still more preferably, the acid-resisting constituent of this invention is used with a photoresist constituent, and in that case, the optical activity compound of the optical activity compound of an acid-resisting constituent and a photoresist constituent is the exposure process of a photoresist layer, and generates the same or almost same acid compound (Mitsuo product), i.e., the Mitsuo product with a desirable similar diffusion property and acid strength, at the time of the exposure to an activation exposure. It is found out that the resolution of the relief image of the finished resist improves further by such matching of an acid-resisting constituent and each photo-oxide product (photoacid products) of a resist. Here, about the "almost same" acid-resisting constituent of this invention, and the photo-oxide product of a resist, the difference of the electric dissociation exponent value (it measures at 25 degrees C) of two Mitsuo products is about 2 or 2.5 or less, the differences of the electric dissociation exponent value of two Mitsuo products are about 1 thru/ or 1.5 or less preferably, and they mean that the difference of the electric dissociation exponent value of two Mitsuo products is about 0.75 or less still more preferably. The difference in such "almost same" molecular weight of an acid-resisting constituent and the photo-oxide product of a resist is 15 or less % of good better \*\*\*\* further about 20 or less % more preferably about 40 or less % still more preferably. furthermore, an acid-resisting constituent and the Mitsuo product of a resist -- for example, both the light product -- a sulfonic acid or both -- halos, such as HBr, -- it is desirable that it is the acid of the same class mutually so that it may be acids. The amount of suitable PAG can be changed very widely and decided easily experientially. Generally, PAG beyond one sort or it of this invention can be suitably used to the total weight of an acid-resisting constituent in about 0.25 to 5 percentage by weight, or the amount not more than it. Please refer to the below-mentioned example about the typical amount used. Moreover, especially the desirable amount of PAG of the acid-resisting constituent of this invention may be changed according to the property and processing conditions of a photoresist which are used with an acid-resisting constituent. For example, when the photo-oxide generating agent of a photoresist generates a comparatively strong acid Mitsuo product and after [ exposure ] baking (PEB) of the photoresist is comparatively carried out at low temperature, since it is harder to pyrolyze the photo-oxide product of an acid-resisting constituent at such low PEB temperature, the effective acid concentration in the inside of an acid-resisting constituent becomes comparatively high. Therefore, the acid-resisting constituent can be effectively blended using a comparatively low-concentration photo-oxide generating agent. On the contrary, when after [ exposure ] baking (PEB) of the photoresist is comparatively carried out at an elevated temperature, as for a part of photo-oxide product of an acid-resisting constituent, a pyrolysis becomes is easier to be carried out. In such a case, in order to secure the effective concentration of an optical generation acid and to make into max reduction of the footing (footing) which is not desirable, a comparatively high-concentration photo-oxide generating agent is blended with an acid-resisting constituent.

[0045] The acid-resisting constituent of this invention may also contain the color compound of the addition which absorbs the exposure light used for exposing the finished photoresist layer again. There is the lubricating agent which a surface lubricating agent is mentioned, for example, is marketed by the trade name of Silwet (Silwet) 7604 from Union Carbide (Union Carbide), or a surfactant FC430 marketed from the three em company (3M) in other additives used if needed. Such a surfactant / a surface lubricating agent are desirable. The concentration of a desirable surfactant is 0.7 - 1.0% in solid content more preferably 0.5 to 15% at solid content. Please refer to the below-mentioned examples 51-55.

[0046] Although the component of an acid-resisting constituent is dissolved in a suitable solvent in order to make a liquefied coating constituent As the solvent, for example Ethyl lactate, Or at least one sort of glycol ether like 2-methoxy ethyl ether (jig rim), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; Methoxybutanol, A solvent with both ether part like an ethoxy butanol, methoxy propanol, and ethoxy propanol, and hydroxy part; Methyl Cellosolve acetate, The ester like ethyl Cellosolve acetate, propylene-glycol-monomethyl-ether acetate, and dipropylene-glycol-monomethyl-ether acetate; they are other solvents like a dibasic acid ester, propylene carbonate, and a gamma butyrolactone at a list.



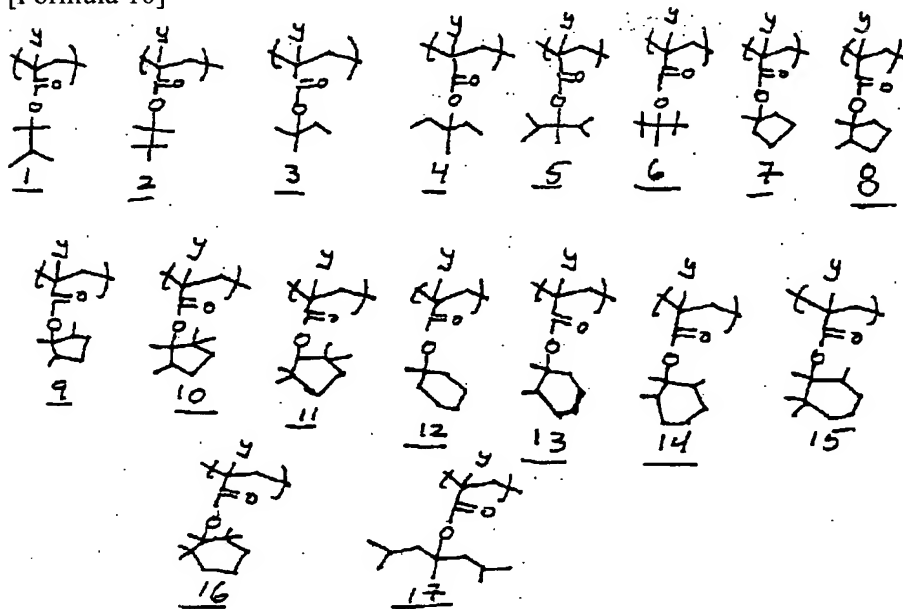
The concentration of the desiccation component in a solvent is decided by some factors [ like ] which are the method of application. Generally, the amount of solid content of an acid-resisting constituent is about 0.5 to 20 percentage by weight of the whole quantity of an acid-resisting constituent, and changes preferably up to about two to 10 percentage by weight of the whole quantity of an acid-resisting constituent.

[0047] Various photoresist constituents including the photo-oxide generating constituent of a positive type and a negative mold can use it with the acid-resisting constituent of this invention. Preferably, ARC of this invention is used with a chemistry magnification positive-resist constituent. Generally the photoresist used with ARC of this invention contains a resin binder and an optical active ingredient.

[0048] Less than 200nm especially of desirable photoresists used with ARC of this invention is designed so that image formation may be carried out on the wavelength of 193nm. The desirable resist constituent used with ARC of this invention is indicated by the United States patent application number 09th by these people submitted on August 28, 1998 / No. 143,462. Especially the desirable resist resin binder used with ARC of this invention has the ester repeat unit containing the non-annular one of five or more carbon or the alkyl group of a single ring like the ester in which the structures 1-17 of a degree type carried out suspension, and two or more the second class carbon or the third class carbon radicals in which photo-oxide susceptibility carried out suspension. the substituent Y shown in the formula -- desirable -- hydrogen or methyl -- it is methyl more preferably.

[0049]

[Formula 10]



[0050] Moreover, the polymer as a resist resin binder component may have other units, such as a cyano group which carried out suspension, and an itaconic-acid-anhydride radical. Preferably, the direct suspension of the itaconic-acid-anhydride part is carried out to a polymer principal chain, namely, the direct suspension of this part is carried out to a polymer joint radical, without having the alkylene group which intervenes between a polymer joint radical and an itaconic-acid-anhydride radical, an aryl group, or other radicals. On the other hand, although the direct suspension of the cyano group is preferably carried out to a polymer principal chain, a joint radical may intervene between a cyano group and a polymer joint radical.

[0051] As long as the polymer used for the resin binder of the resist of this invention is a request, it may contain units, such as a radical which contributes to the drainage system development nature of a photoresist further. For example, as a desirable polymer radical which contributes to drainage system development nature, acrylic-acid, methacrylic-acid, and methacrylic-acid-2-hydroxyethyl, a carboxy part which is obtained by the polymerization of other monomers, or a hydroxy part is mentioned. As other desirable polymer units, the unit acquired by polymerizations, such as vinyl alicyclic radicals, such as methacrylic-acid-2-adamantyl-2-methyl and methacrylic-acid isobornyl, or an un-annular alkyl group like t-butyl methacrylate, for example is included. Generally, the desirable acid susceptibility (acid labile) polymer used for the chemistry magnification photoresist of this invention has one or more polymerization units of the

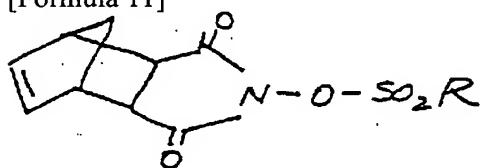
monomer of methacrylic-acid isobornyl, a methacrylonitrile, itaconic acid anhydride, a methacrylic acid, t-butyl methacrylate, methacrylic-acid-2-methyl-2-adamantyl or a methacrylic acid -2, and 3-dimethyl-2-butyl.

[0052] The sulfonate photo-oxide generating agent which included sulfonation ester and sulfonyl oxyketone in a non-ion system organic light activity compound like the halogenation light activity compound currently indicated by U.S. Pat. No. 5,128,232 (Thackeray, et al.) which is indicated by this invention at U.S. Pat. No. 4,442,197 by which the citation publication is carried out, No. 4,603,101, and No. 4,624,912 as a photo-oxide generating agent compound of the suitable resin used with ARC of this invention, such as an onium salt and Thackeray, and the list is mentioned. Please refer to "journal OBU photopolymer Science and technology" (340 J. of Photopolymer Science and Technology, 4(3):337- 1991) about the indication of the suitable sulfonate PAG containing benzoin tosylate, t-butylphenyl alpha (p-toluenesulfonyloxy)-acetate, and t-butyl alpha (p-toluenesulfonyloxy)-acetate. The desirable sulfonate PAG is indicated by U.S. Pat. No. 5,344,742 of a sinter (Sinta, et al.).

[0053] As suitable PAG for photoresists used with ARC of this invention, the imide sulfonates like the compound of a degree type are mentioned.

[0054]

[Formula 11]

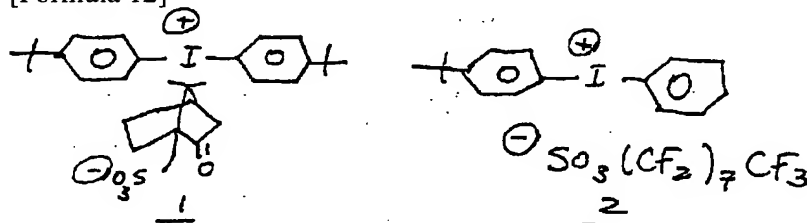


[0055] (R is perfluoro-alkyls, such as perfluoro-[ camphor, adamantane, alkyl (for example, one to C12 alkyl), and ] (one to C12 alkyl), especially a perfluoro-octane sulfonate, a perfluoro-nonane sulfonate, etc. among a formula.) Especially desirable PAG is N-[(perfluoro-octane sulfonyl) oxy]-5-norbornene -2 and 3-dicarboxyimide.

[0056] Moreover, PAG1 and PAG2 of a degree type are suitable as resin used with ARC of this invention.

[0057]

[Formula 12]



[0058] Such a sulfonate compound is prepared as indicated by the European Patent application No. (public notice number No. 0783136) 961181112 which is describing composition of the above PAG 1 in the detail. If an outline is described, PAG1 trickles a sulfuric acid into the mixture of a potassium iodate, t-butylbenzene, and an acetic anhydride, it will be made to react, cooling by the ice bath, and will be prepared. Subsequently, a reaction mixture is agitated at a room temperature for about 22 hours, and water is added, and it cools to about 5-10 degrees C, and, subsequently washes by the hexane. Then, the water solution of diaryl iodonium and a hydrogensulfate is cooled to about 5-10 degrees C, a camphor sulfonic acid is added, and ammonium hydroxide neutralizes further.

[0059] Moreover, said two sorts of iodonium compounds in which the anions and complexes other than the above-mentioned camphor sulfonate radical and a perfluoro-octane sulfonate radical were formed are also suitable. Especially, as a desirable anion, what is shown by formula RSO3- is mentioned. R is other perfluoro-alkyls, such as perfluoro-[ adamantane, alkyl (for example, one to C12 alkyl), and ] (one to C12 alkyl), especially a perfluoro-butane sulfonate, etc. among a formula.

[0060] Other well-known PAG can be used into the resin used according to this invention. It is PAG which does not have an aromatic series radical like the above-mentioned imide sulfonate for 193nm image formation in order that desirable one may generally raise the transparency of a resist.

[0061] If it is a request, as a desirable additive of the resin of this invention, an addition base, the tetrabutylammonium hydroxide (TBAH) which raises the resolution of the resist relief image developed



especially, or lactic-acid tetrabutylammonium will be mentioned. It is hindered amine [ like a diazo bicyclo undecane or diazo bicyclo nonene to the resist which carries out image formation by 193nm ] whose desirable addition base is. an addition base -- for example, about 0.03 to 5 percentage by weight of total solids -- small quantity is used comparatively suitably.

[0062] If the photoresist of this invention is a request, it can contain other matter again. For example, a striation inhibitor, a plasticizer, an accelerating agent, etc. are mentioned as other additives as occasion demands. For example, as for the additive used such if needed except for a bulking agent and a color with a thing like the amount of about five to 30 percentage by weight of the total weight of a resist desiccation component comparatively existed by high concentration, it is common to exist in a photoresist constituent by low concentration.

[0063] ARC of this invention which contains a cross linking agent whenever [ like suitable glycouril / low-salt radical ] is useful especially if a strong acid Mitsuo product like a triflic acid, sulfonic-acid camphor, other sulfonic acids, or other acids with about two or less electric dissociation exponent (25 degrees C) is used with the photoresist generated at the time of exposure. Since there is quite little optical type-of-seasonal-prevalence strong acid which moves from a resist and remains into an ARC layer compared with ARC of the congener containing a more basic cross linking agent, without being bound by the theory, if ARC(s) of this invention are used with such a strong acid resist, it will be thought especially that it is effective. That is, a cross linking agent has few extent of association with the optical type-of-seasonal-prevalence strong acid of the finished resist layer compared with a more basic ARC cross linking agent whenever [ low-salt radical / of this invention ]. Consequently, disappearance of an acid decreases from a resist layer and it is avoided whether the problem of resolution like a potential footing (footing) decreases.

[0064] In use, the acid-resisting constituent of this invention is applied to a substrate as a spreading layer by either of various approaches like spin coating. An acid-resisting constituent is usually preferably applied to a substrate by the thickness of about 0.04 and the desiccation layer between 0.20 micrometers in the thickness of about 0.02 and the desiccation layer between 0.5 micrometers. The substrate is suitable at any substrate currently used from the former in the process relevant to a photoresist. For example, as this substrate, the micro electronic wafer of silicon, diacid-ized silicon, or an aluminum-aluminum oxide etc. is possible. Gallium arsenide, a ceramic, a quartz, or a copper substrate may also be used. The substrate used for monotonous panel displays, such as a liquid crystal display or a glass substrate, and an indium tin oxide coating substrate, is also used.

[0065] Preferably, before a photoresist constituent is applied on ARC, it is good to harden an acid resistibility layer. Hardening conditions change with ARC components. Therefore, when this constituent does not contain an acid or an acid generator, curing temperature and conditions are severer than the case of the constituent containing an acid or an acid generator compound. Typical hardening conditions are for about 0.5 - 40 minutes at about 120 degrees C - 225 degrees C. The hardening conditions which make not only an alkaline development water solution but a photoresist solvent insolubilize an ARC coating layer substantially are desirable.

[0066] After such hardening, a photoresist is applied on the surface of ARC. A photoresist can be applied like spreading of ARC with any usual means so that according to rotation, immersion, a meniscus (meniscus), or roll coating. Generally after spreading dries a photoresist coating layer with heating, and it removes a solvent until a resist layer becomes non-adhesiveness preferably. It should be made for an ARC layer and a photoresist layer not to be mixed mutually in essence the optimal.

[0067] Next, an image is made to form in a resist layer by activation exposure through a mask by the conventional approach. In order to activate the optical active ingredient of a resist system effectively, the image patternized by the resist coating layer is formed by sufficient exposure energy. In more detail, although exposure energy is based on an exposure device, generally it is the range of about 3 to 300 mJ/cm<sup>2</sup>. the difference of the solubility between the field where the coating layer was exposed, and the field which is not exposed is made, or in order to boil the difference greatly and to carry out it, baking after exposure may be given to the exposed resist layer. For example, in order that the acid hardening mold photoresist of a negative mold may carry out induction of the acid promotion mold crosslinking reaction, generally heating after exposure is needed, and on the other hand, many chemistry magnification mold positives resist need heating after exposing in order to perform an acid promotion mold deprotection reaction. general -- as the baking conditions after exposure -- the temperature of about 50 degrees C or more -- the temperature of the range of about 50 degrees C - 160 degrees C is mentioned in more detail.

[0068] Subsequently, although the exposed resist enveloping layer is developed, it is desirable to use an aquosity developer like the inorganic alkali which makes an example organic alkali like the example of

tetrabutylammonium hydroxide or a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium hydrogencarbonate, a sodium silicate, a meta-sodium silicate, aqueous ammonia, etc. An organic developer can be used as an option. Generally, development is based on the approach well learned to this contractor.

[0069] Next, the developed substrate can etch or plate chemically the substrate field where the photoresist was exposed to the substrate field to which the photoresist was exposed by alternative processing, for example, this contractor, according to the well-known procedure. As a suitable etching agent, a hydrofluoric-acid etching solution and a plasma gas etching agent like an oxygen plasma-etching agent are mentioned. A plasma gas etching agent removes the antihalation coating layer over which the bridge was constructed.

[0070]

[Example] All the reference stated by this invention is referred to in this invention. The following examples do not illustrate this invention and do not limit it.

[0071] Example 1-3 : Synthetic example of a polymer 1 : The mole ratio compounded the 3 yuan copolymer which consists of the monomer of the styrene and methacrylic-acid-2-hydroxyethyl which are 30:38:32, and a methyl methacrylate with the following procedures. The monomer (styrene of 99% of Aldrich purity 169.79g; 173.97g of methyl methacrylates by methacrylic-acid-2-hydroxyethyl 269.10g; the loam, and HASU of "ROKURIRU 400 (Rocryl400)" made from loam and HASU) was dissolved in 2,375g THF in the up agitator, the condenser, and the 3 opening round bottom flask of 5L which attached the nitrogen inlet. Nitrogen was poured for 20 minutes in the reaction solution, and degasifying was performed. 11.63g of Du Pont initiators Vazo52 was added to the solution, and it maintained at this temperature for 15 hours, performing a heating ring current (65 to 67 degree C). After cooling a reaction solution to a room temperature, it was made to precipitate in MTBE/cyclohexane (volume/volume 1/1) 12L. Polymers were collected with vacuum filtration and it dried in the 48-hour vacuum at 50 degrees C. Yield is 68% and subsequent analysis showed that residual monomers were 2.4 % of the weight, Tg=92 degree C, and Td=239 degree C. The percentage of the mol concentration of BAZO 52 initiator to the sum total of the mol concentration of a monomer was 0.72%. The molecular weight analysis by gel permeation chromatography (gel permeation chromatography) showed that it was Mw=22,416 and Mn=10,031.

[0072] Example 2-3 : The copolymer of 3 yuan with an another styrene:methacrylic-acid-2-hydroxyethyl:methyl methacrylate was compounded like the procedure of an example 1 except having changed mol % of the amount of injection monomers according to the following.

Example 2 : Polymer compounded by the ratio 12:38:50 of mol %. t-butyl methyl ether (5,000mL) was used as a precipitate solvent. Yield was 168g (84% of a theoretical value). The results of the molecular-weight analysis by gel permeation chromatography are Mw=19,612 and Mn=10,434 in a relative value with the correlation sample of polystyrene, and it turned out that they are Tg=76 degree C and Td=201 degree C as a result of subsequent analysis.

[0073] Example 3 : 3 yuan copolymer which consists of the styrene, the methacrylic-acid-2-hydroxyethyl, and the methyl-methacrylate monomer of the mol % ratio 18:38:44. The hexane (4,500mL) was used as a precipitate solvent. Yield was 68g (79% of a theoretical value). The results of the molecular-weight analysis by gel permeation chromatography are Mw=22,712 and Mn=11,564 in a relative value with the correlation sample of polystyrene, and it turned out that it is Tg=107 degree C as a result of subsequent analysis.

[0074] Example 4 : According to the procedure of an example 1, the 3 yuan copolymer of a styrene:methacrylic-acid-2-hydroxyethyl:methyl methacrylate was compounded by the mol % ratio 30:38:32 of a monomer using the 0.36-mol % of initiator Vazo52. The results of the molecular-weight analysis by gel permeation chromatography were Mw=54,502 and Mn=22,495 in the relative value with the correlation sample of polystyrene.

[0075] Example 5 : According to the procedure of an example 1, the 4 yuan copolymer of styrene:methacrylic-acid-2-hydroxyethyl:methyl-methacrylate:n-butyl methacrylate was compounded by the mol % ratio 30:38:31:1 using the 0.72-mol % of initiator Vazo52. The results of the molecular-weight analysis by gel permeation chromatography are Mw=22,646 and Mn=10,307 in a relative value with the correlation sample of polystyrene, and it turned out that they are Tg=74 degree C and Td=331 degree C as a result of subsequent analysis.

[0076] Example 6 : According to the procedure of an example 1, the 3 yuan copolymer of a 4-acetoxy styrene:methacrylic-acid-2-hydroxyethyl:methyl methacrylate was compounded by the mol % ratio 18:38:44 using the 0.36-mol % of initiator Vazo52. Polymer yield was 84%. The results of the molecular-weight analysis by gel permeation chromatography are Mw=73,888 and Mn=29,973 in a relative value with

the correlation sample of polystyrene, and it turned out that they are  $T_g=74$  degree C and  $T_d=247$  degree C as a result of subsequent analysis.

[0077] Example 7 : According to the procedure of an example 1, the 3 yuan copolymer of a methacrylic-acid phenyl:methacrylic-acid-2-hydroxyethyl:methyl methacrylate was compounded by the mol % ratio 30:38:32 using the 0.36-mol % of initiator Vazo52. Yield was 94%. The results of the molecular-weight analysis by gel permeation chromatography are  $M_w=111,039$  and  $M_n=26,866$  in a relative value with the correlation sample of polystyrene, and it turned out that they are  $T_g=91$  degree C and  $T_d=242$  degree C as a result of subsequent analysis.

[0078] Example 8 : According to the procedure of an example 1, the 3 yuan copolymer of a methacrylic-acid benzyl:methacrylic-acid-2-hydroxyethyl:methyl methacrylate was compounded by the mol % ratio 18:38:44 using the 0.91-mol % of initiator Vazo52. Polymer yield was 99%. The results of the molecular-weight analysis by gel permeation chromatography were  $M_w=21,614$  and  $M_n=11,379$  in the relative value with the correlation sample of polystyrene.

[0079] example 9 : the procedure of an example 1 -- following -- 0.91-mol % of an initiator (BAZO 52) -- using -- a mol -- the 3 yuan copolymer of a methacrylic-acid-2-phenylethyl:methacrylic-acid-2-hydroxy:methyl methacrylate was compounded by the % ratio 18:38:44. Polymer yield was 98%. The results of the molecular-weight analysis by gel permeation chromatography were  $M_w=29,008$  and  $M_n=15,956$  in the relative value with the correlation sample of polystyrene.

[0080] Example 10 : According to the following procedures, the antireflection coating (ARC) constituent was prepared using the polymer of an example 1. Polymer 1.2175g of an example 1, tetramethoxy methyl GURIKORURIRU(American cyanamide company make) 0.225g, 0.0075g of p-toluenesulfonic acid, FC-430 (3 M company make) 0.0135g, JI (4-t-buthylphenyl) iodonium Perfluoro-octane sulfonate (product made from DEIKEMU) 0.0965g, and propylene glycol Weighing capacity of the monomethyl ether alcohol ("Dowanol PM", Dow-Jones company make) 48.44g was carried out, and it put into the bottle of 100mL(s), it placed on the roller, and the dissolution was promoted. After dissolving, the ARC constituent was filtered through the Teflon filter (0.1 micrometers or 0.2 micrometers), and it put into the pure bottle.

[0081] Example 11 : According to the following procedures, the antireflection coating (ARC) constituent was prepared using the polymer of an example 1. Polymer 1.2175g of an example 1, tetramethoxy methyl GURIKORURIRU(American cyanamide company make) 0.150g, 0.075g ("Cymel303") of hexamethoxy melamine mixture, 0.0075g of p-toluenesulfonic acid, FC-430 (3 M company make) 0.0135g, JI (4-t-buthylphenyl) iodonium monomethyl ether alcohol Perfluoro-octane sulfonate (product made from DEIKEMU) 0.0965g, and propylene glycol ("Dowanol PM" --) Weighing capacity of the 48.44by Dow-Jones company g was carried out, and it put into the bottle of 100mL(s), it placed on the roller, and the dissolution was promoted. After dissolving, the ARC constituent was filtered through the Teflon filter (0.1 micrometers or 0.2 micrometers), and it put into the pure bottle.

[0082] Example 12 : According to the following procedures, the antireflection coating (ARC) constituent was prepared using the polymer of an example 1. Polymer 4.571g of an example 1, tetramethoxy methyl GURIKORURIRU(American cyanamide company make) 0.8438g, p-nitrobenzyl tosylate 0.0281g, FC-430 (3 M company make) 0.0450g, JI (4-t-buthylphenyl) iodonium Weighing capacity of perfluoro-octane sulfonate (product made from DEIKEMU) 0.1371g and the propylene-glycol-monomethyl-ether alcoholic ("Dowanol PM", the Dow-Jones company make) 48.44g was carried out, and it put into the bottle of 500mL (s), it placed on the roller, and the dissolution was promoted. After dissolving, the ARC constituent was filtered through the Teflon filter (0.1 micrometers or 0.2 micrometers), and it put into the pure bottle.

[0083] Example 13 : According to the following procedures, the antireflection coating (ARC) constituent was prepared using the polymer of an example 1. Polymer 1.314g, tetramethoxy methyl GURIKORURIRU (American cyanamide company make) 0.225g, 0.0075g of p-toluenesulfonic acid, FC-430 (3 M company make) 0.0135g, and propylene glycol of an example 1 Weighing capacity of the monomethyl ether alcohol ("Dowanol PM", Dow-Jones company make) 48.44g was carried out, and it put into the bottle of 100mL(s), it placed on the roller, and the dissolution was promoted. After dissolving, the ARC constituent was filtered using the Teflon filter (0.1 micrometers or 0.2 micrometers), and it put into the pure bottle.

[0084] Example 14-18 : Except having changed the amount of p-toluenesulfonic acid and tetramethoxy methyl GURIKORURIRU, the acid-resisting constituent was prepared using the example 13, the very similar procedure, and the presentation. The percentage by weight of these [ to the whole quantity of the solid content in a constituent ] two components is shown in Table 1.

[0085]

表 1 : A R C 組成物

実施例	テトラメトキシメチルグリコリル	p-トルエンスルホン酸
	固形分重量%	固形分重量%
1 4	1 2	0 . 1
1 5	1 8	0 . 1
1 6	1 5	0 . 3
1 7	1 2	0 . 5
1 8	1 8	0 . 5

[0086] Example 19-23 Except having changed the amount of FC430, the acid-resisting constituent was prepared using the example 13, the very similar procedure, and the presentation. The percentage by weight of this component to the whole quantity of the solid content in a constituent is shown in Table 2.

[0087]

表 2 : A R C 組成物

実施例	FC430 固形分重量%
1 9	0 . 2
2 0	0 . 5
2 1	0 . 8
2 2	1 . 1
2 3	2 . 0

[0088] Example 24-25 : The weight of each component in a constituent is made to be the following. The acid-resisting constituent was prepared using the example 13, the very similar procedure, and the presentation. : Polymer 0.6102g, tetramethoxy methyl GURIKORURIRU(American cyanamide company company make) 0.1125g, 0.0030g of p-toluenesulfonic acid, FC-430 (3 M company make) 0.0060g, JI (4-t-buthylphenyl) iodonium Perfluoro-octane sulfonate (product made from DEIKEMU) 0.0183g, and propylene glycol Monomethyl ether alcohol ("Dowanol PM", Dow-Jones company make) 24.25g. These constituents are indicated to Table 3.

[0089] Table 3: ARC constituent example Example 24 of the used polymer 825 9 [0090] Example 26-32 : The weight of each component in a constituent is made to be the following. The acid-resisting constituent was prepared using the example 13, the very similar procedure, and the presentation. : Polymer 0.974g, tetramethoxy methyl GURIKORURIRU(American cyanamide company company make) 0.180g, 0.0060g of p-toluenesulfonic acid, FC-430 (3 M company make) 0.0108g, JI (4-t-buthylphenyl) iodonium Perfluoro-octane sulfonate (product made from DEIKEMU) 0.0292g, and propylene glycol Monomethyl ether alcohol ("DowanolPM", Dow-Jones company make) 38.80g. These constituents are indicated to Table 4.

[0091] Table 4: ARC constituent example The example 26 of the used polymer 127 428 629 730 231 332 5

[0092] Example 33-35 : Spin coating of the optical test ARC constituent of an ARC constituent was carried out on 200mm Si wafer, and baking was performed for 90 seconds at 215 degrees C on 150 micrometer contiguity hot plate of non-contact types using new style FSI wafer spreading Rhine (wafer coating track). The ARC film was measured using the Warren polarization analysis mold refractive-index meter (Wollem ellipsometer) (Lincoln NE), and the quantum of the optical refractive indexes n and k in 193nm (it is actual reaching imagination) was carried out. The refractive index of imagination is correlated with the membranous absorbance. : In order to minimize the reflection factor of a membranous lap, minimizing ARC thickness, the value of k needs to be 0.3 or more. The most desirable value of k is about 0.4 or more. These values are indicated to Table 5.

[0093]

表 5 : 193 nm で測定した A R C 組成物の光学パラメーター

実施例	実際の屈折率 $n$	仮想の屈折率 $k$
シップレー A R 2 (シップレー社製)	1. 7 0	0. 1 0
3 3	1. 7 3	0. 2 1 6
3 4	1. 7 4	0. 2 9 5
3 5	1. 7 7	0. 4 0

[0094] These data show that it has the refractive index of remarkable low imagination compared with the value desired in order that the cypridium rhe AR 2 which is a comparison ingredient, i.e., the ARC ingredient for commerce which is designed in order to use it in 248nm, and is used widely, may minimize a reflection factor in 193nm. These data show that k value of a constituent 30-32 increases again, so that the phenyl part in a polymer (introduced through the styrene monomer in this case) increases. A phenyl group is a good chromophore in 193nm, and this invention persons believe that he can obtain the refractive index of desirable imagination, and k by choosing the ideal concentration of the phenyl group in a polymer.

[0095] Example 36-40 : The insoluble evaluation ARC film of ARC behind baking is strongly wanted to harden between coating and a baking process and to become an insusceptibility in a subsequent lithography (lithography) processing phase to the photoresist by which coating is carried out succeeding as a result. In this invention, hardening of ARC in baking is attained through bridge formation by the chemical acid catalyst of a polymer. Lithography processing without the newest defect used especially in semi-conductor manufacture does not have Society for Cutting Up Men (scum), residue, and the flare (flare) in the interface of the pattern of a resist, and an ARC coating substrate as much as possible, and it is being required that the sharpness of an image edge excellent in one side should be maintained. The pattern of a resist must be pasted up well between [ ARC ] the phases of a lithography process again. both the ARC film that this invention persons hardened with the resist in order to fill these demands -- being mixed -- it is believed that-izing should be carried out [ minimum ] as much as possible. About the ARC film which some hardened, it considered quantifying whether it has the susceptibility over the dissolution or swelling in the ethyl lactate which are those typical solvents for resist coatings currently used commercially. Therefore, the ARC constituent was coated on Si, baking was performed for 60 seconds at 215 degrees C, and the film with a thickness of 60nm was obtained. Thickness was measured by 11 places using the nano metrics (Nanometrics) 215AFT thickness measurement machine. Subsequently, the ARC spreading wafer was immersed in the beaker into which the ethyl lactate solvent was put for 60 seconds. The wafer was air-dried, after being water and failing to rinse ethyl lactate. Thickness was measured in the same part using the same measuring instrument, and change of thickness was recorded. A result is shown in Table 6.

[0096]

表 6 : 乳酸エチル中 6 0 秒浸漬後の A R C 膜厚の変動

実施例	レジスト組成物	漬後後の厚み変化 (＊)	コメント
3 6	1 4	4 4 ＊減少	膜の変色
3 7	1 5	3 4 ＊減少	膜の変色
3 8	1 6	0 ＊	良好品質
3 9	1 7	0 ＊	良好品質
4 0	1 8	0 ＊	良好品質

＊：単位はオングストローム

[0097] As for an example 38-40, constituents 16, 17, and 18 show that it is an insusceptibility to either the

dissolution or swelling in an ethyl lactate solvent. This affirmative result suggests what the interface clear as a result will be formed for between a resist pattern and the ARC film between the pattern formation by lithography with these standard constituents. The example 36-37 shows some dissolutions of ARC in the resist solvent, and lithography processing came out not good about 38 to 40 example, and it has suggested a certain thing. The constituent 16-18 had the concentration (0.3%-0.5%) of a high acid by the inside of the original ARC constituent compared with the examples 14 and 15 with the lower (0.1%) concentration of toluenesulfonic acid. As a result, the concentration of the desirable acid in an ARC constituent is larger than 0.1%, and is 0.3% or more more preferably. Although it does not adhere to the theory, it is believed that higher acid concentration brings about high crosslinking density rather than it can set on the ARC film in baking, and it makes the film an insusceptibility more to the attack of a solvent. Therefore, the concentration of at least 0.3% of toluenesulfonic acid was used for evaluation of future ARC ingredients and a constituent.

[0098] Example 41-42 : Resist constituent perphloro-octane sulfonate-norbornene dicarboxyimide 0.524g used for the performance evaluation of ARC, JI (4-t-buthylphenyl) iodonium The combination of perfluoro-octane sulfonate (DTBIPFOS) 0.0449g and a binder polymer a 1 and 8-diazabicyclo [5, 4, 0] undeca-7-en (the Aldrich make --) 0.0045g of U.S., and Silwet 7604 (Silwet [7604 ] and the Dow Corning make --) By dissolving into the stock solution containing 0.0075g of U.S., and propylene glycol methyl ether acetate (Dow-Jones company make, U.S.) 43.5g, the suitable photoresist constituent for a lithography test was prepared. In order to promote the dissolution of DTBIPFOS, this compound was added to the resist constituent as a 5% solution of ethyl lactate. After dissolving, the resist constituent was filtered through the Teflon filter (0.1 micrometers or 0.2 micrometers), and it put into the pure bottle.

[0099] Example 41 : The binder polymer obtained by making the supply mole ratio of methacrylic-acid isobornyl:t-butyl methacrylate:methacrylic-acid:methacrylonitrile:itaconic acid anhydride the indicated resist constituent 31:22:10:14:23 was used. The following procedures adjusted this polymer. The anhydrous tetrahydrofuran of 12.54g [ of itaconic acid anhydride ], 15.20g [ of t-butyl methacrylate ], and methacrylonitrile 4.58g, 4.28g [ of methacrylic acids ], and methacrylic-acid isobornyl 33.57g and 100mL(s) was put into the flask of 500mL(s). The purity of all reagents was at least 99%. The magnetic type stirring rod, the condensation machine, and the wax for pouring were attached in the flask. In advance of the reaction, all the components were purged for 20 minutes with nitrogen gas. The free radical initiator 52 and Vazo 0.75g and anhydrous tetrahydrofuran 25mL were put into the wax for pouring. The temperature up of the solution was carried out to 70 degrees C, and, subsequently the initiator was poured over 20 minutes. The flask was kept at 70 degrees C for 14 hours, and it cooled to the room temperature after that. It was made to precipitate in the hexane of 3L, it dried in the Buchner wax and (Buchner funnel), and the polymer was obtained. Subsequently, the polymer was remelted in the acetone of 120mL(s), and it reprecipitated in the hexane of 3L, and brought together in the Buchner wax and the top. Overnight desiccation of the polymer was carried out at the room temperature in vacuum oven. Yield was 49.96g (66%).

[0100] Example 42 : The binder polymer obtained by making the supply mole ratio of the methacrylic-acid isobornyl:methacrylic acid -2 and 3-dimethyl butyl:t-butyl methacrylate:methacrylic-acid:methacrylonitrile:itaconic acid anhydride the indicated resist constituent 15:10:28:10:14:23 was used. The following procedures adjusted this polymer. The procedure similar to an example 41 adjusted this polymer. A methacrylic acid -2 and 3-dimethyl butyl were compounded with the following procedures. It put into the flask of 500mL(s) which put in the stirring rod for tetrahydrofuransg [ 180 ] and 2 and 3-dimethyl-1-butanol 40g and anhydrous triethylamine 40.93g, and attached the condensation machine under N2 ambient atmosphere. It added, while methacrylic-acid chloride 40.927g refined to this was dropped from the wax for pouring. It reacted by heating quietly. After stirring for 24 hours, the tetrahydrofuran was evaporated from the solution using the rotating type evaporator, and the ethyl acetate of 100mL was added. Subsequently, the salt was carried out the \*\* exception through the Buchner wax. Use of a rotating type evaporator removed ethyl acetate. The vacuum distillation cylinder equipped with a 8 inches BIGURO column (Vigreux column), a stirring rod, and some small zeolites was prepared. Fractional distillation was carried out and 19.8g of products was collected as a fraction which has the boiling point of about 80 to 87 degree C under the pressure of 6 to 7 torrs. Structure and purity were checked using <sup>1</sup>HNMR.

[0101] Example 43-64 : In order to evaluate the engine performance of the pattern formation resolution by the lithography of the resist on an ARC constituent, the property which used high-pressure cross-section scanning electron microscopy, and was able to be burned was inspected. The degree of minimum solution image in the grid image of the pitch of 1:1 When the 160nm line of 1:1 and the 160nm tooth space which were formed on the mask choose light exposure which is substantially measured with the dimension of

160nm actually, respectively. Subsequently, it evaluated by measuring that the line (full-thickness line) of the min which held predetermined thickness substantially developed by clarification has a smooth crowning, and residue does not remain on a substrate. A sensitization rate is expressed with light exposure required to form such a pattern. It turns out that a sensitization rate does not change remarkably even if ARC constituents differ. The resist constituent of an example 41 showed the sensitization rate of about 29 mJ/cm<sup>2</sup>, and the resist constituent of an example 42 showed the sensitization rate of about 24 mJ/cm<sup>2</sup>. On the newest wafer processing equipment (EFUESUAI and S buoy G company (FSI and SVG Companies) make), lithography processing was carried out using the both sides of a silicon wafer (150mm and 200mm). All processings were performed in the ambient atmosphere which does not have a basic pollutant substantially (a measurement amine / less than [ ammonia 5ppb ]). The ARC constituent was applied to the wafer in advance of subsequent processing. The spin coat of the ARC film was carried out with a suitable rotational speed chosen so that the thickness of about 65nm might be given, and it baked at 215 degrees C. The spin coat of the photoresist was carried out on the wafer by about 3,000 rpm, baking was performed on 150 micrometer contiguity hot plate (proximity-gap plate) of non-contact types (spreading postcure (PAB)), it cooled to the room temperature quickly after that, and 4,200Å thickness was obtained. Subsequently, to this film, it is GCA0.60NA. On ArF (193nm) wafer Tepper, it exposed by partial coherence (coherence) setup 0.70 using the resolution test pattern. After that, immediately, baking was performed on 150 micrometer contiguity hot plate of non-contact types (exposure postcure (PEB)), and this film was quickly cooled to the room temperature. This film was immediately developed with 0.26-N tetramethylammonium hydroxide developer of British Standard after that at the 60-second single paddle type process (60 second track-single-puddle process) of British Standard.

[0102] Table 7: Lithography test-result ResL of the resist constituent on ARC expresses the resolution in Es. PAB and PEB are the units of \*\*, and ResL is expressed with the unit of nm. DUV-18J are the ARC product currently used commercially, it is marketed from BURYUWA Saiensu-Sha (Brewer Sciences Incorporated) of Missouri, and AR2 is an ARC product which is marketed from the cypripedium rhe company (Shipley Company) of Massachusetts, and is used commercially.

[0103]

実施例	ARC 実施例	レジスト 実施例	P A B	P E B	R e s L	レジスト断面 コメント
44-比較	DUV18J	41	140	155	>160	スカム不良; フレア
45-比較	AR2	41	140	155	N/A	レジスト接着不良
46	10	41	140	155	150	エッジ鋭さ良好
47	11	41	140	155	150	エッジ鋭さ良好
48	12	41	140	155	150	エッジ鋭さ良好
49	13	42	140	150	140	エッジ鋭さ良好
50	16	41	140	155	150	僅かなスカム
51	19	41	140	155	150	僅かなスカム
52	20	41	140	155	150	極く僅かなスカム
53	21	41	140	155	150	エッジ鋭さ良好

[0104]

表 7 (続き)

54	22	41	140	155	150	極く僅かな細り
55	23	41	140	155	150	僅かな細り
56-比較	24	41	140	155	160	フレアおよびスカム
57-比較	25	41	140	155	155	フレアおよびスカム
58	26	41	140	155	150	エッジ鋭さ良好
59	27	41	140	155	150	エッジ鋭さ良好



60	28	41	140	155	150	エッジ鋭さ良好
61	29	41	140	155	150	エッジ鋭さ良好
62	30	41	140	155	150	エッジ鋭さ良好
63	31	41	140	155	150	エッジ鋭さ良好
64	32	41	140	155	150	エッジ鋭さ良好

[0105] The constituent of consideration this invention of an example 17-32 can bring about suitable remarkable highly efficient ARC(s) for the manufacture application of a semi-conductor. the quality of the interface between a resist pattern and an ARC under-coating layer -- more -- clear -- more -- residue -- few -- and ARC constituent 46- the resolution of 49, 53, and 58-61 has exceeded the resolution of DUV-18J which are the conventional ARC ingredient, and AR2. ARC constituent 46- the engine performance of 49, 53, and 58-61 has exceeded the engine performance of the examples 56 and 57 for a comparison again. constituent 46- the engine performance which was excellent in 49, 53, and 58-61 shows again that the best result is obtained, when a polymer does not have alkyl mediation group (alkyl spacer group) structure between a polymer chain and a phenyl chromophore (for example, methacrylic-acid benzyl in the methacrylic-acid phenyl in an example 56, or an example 57).

[0106] Example 65: The first purpose which uses ARC in the test lithography process of the reflex inhibition is minimizing the fluctuation looked at by the observation sensitization rate as it changes minimizing the "oscillating curve" ("swing curve") of a resist, i.e., the thickness of a resist. In order to evaluate the reflex inhibition, the resist of an example 49 was processed by the lithography-technique on ARC of an example 13 according to the process of an example 44-64, and the same process. However, ARC thickness was kept at 82.5nm as an exception, and the thickness of the resist film was changed into 500nm from 400nm by changing the rate of spin coating. The light exposure (E0) which pattern formation takes as a sensitization rate was measured. The data is shown in the following table 8.

[0107]

Table 8: Sensitization rate of surveyed resist, and E zero-pair example 13 The resist thickness on ARC Resist thickness (nm) A sensitization rate, E0 (mJ/cm<sup>2</sup>) 402 7.8 412 7.7 423 7.5 429 7.5 463 8.0 471 7.9 492 7.8 [0108] The greatest range of fluctuation in fluctuation of Esurveyed 0 is 8.0-7.5=0.5 mJ/cm<sup>2</sup>. This is fluctuation of a very small sensitization rate, and is permitted also to almost all the newest lithography process. This small value shows that the constituent of this invention is effective in controlling reflection of the light from a substrate during the exposure in 193nm.

[0108] The greatest range of fluctuation in fluctuation of Esurveyed 0 is 8.0-7.5=0.5 mJ/cm<sup>2</sup>. This is fluctuation of a very small sensitization rate, and is permitted also to almost all the newest lithography process. This small value shows that the constituent of this invention is effective in controlling reflection of the light from a substrate during the exposure in 193nm.

[0109] The old publication of this invention can make modification and correction, without separating from the range or pneumonia of this invention so that it may be for only illustrating it and may explain in the following claims.

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[Translation done.]



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